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CALCULATIONS OF CHEMICAL EQUILIBRIA

Examples and Problems

Mir Publishers Moscow

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РАСЧЁТЫ ХИМИЧЕСКИХ РАВНОВЕСИЙ

Сборник примеров и задач

*Под редакцией
проф. Г. М. Панченкова*

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V. A. Skoblo

CALCULATIONS OF CHEMICAL EQUILIBRIA

Examples and Problems

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Preface

The main object of this training aid is to teach students how to calculate chemical equilibria. A chemical engineer must be able to calculate whether or not a given chemical process will proceed, determine the stability of substances in given external conditions, compute the equilibrium and, consequently, the maximum yields of the products in given conditions, and find the optimal external parameters for conducting a process.

We have given great attention to calculating the heats of chemical reactions, heat capacities, entropies, and fugacities. Apart from problems involving the direct application of the fundamental laws of chemical thermodynamics, the book contains interesting examples showing various empirical and approximate methods of calculations. For instance, space is devoted to calculations of the heats of combustion by the methods of D. Konovalov, M. Kharasch, of increments, of introducing corrections for the substitution of hydrogen by methyl and other groups, of P. Maslov, J. Franklin, M. Souders, C. Matthews, and C. Hurd. Approximate methods, which play a great part in engineering calculations of chemical processes, are considered for heat capacities, standard entropies, and Gibbs energies.

A large section is devoted to calculating the change in the Gibbs energy as a result of chemical reactions and of the compositions of equilibrium mixtures. Since in practical work one often has to do with non-ideal systems, we have set out the basic methods of calculating fugacities, as well as the use of fugacities and activity coefficients for determining the equilibrium composition of a mixture of non-ideal systems. We have also described empirical methods of calculating the critical parameters (the method of A. Lydersen, J. Forman, and G. Thodos), and the calculation of enthalpies and heats of reactions conducted at high pressures.

We begin each chapter with a brief theoretical introduction treating the main formulas needed for solving the problems. The introduction is given only to remind our readers of the basic laws used in solving the problems, and cannot in any way replace a textbook

in chemical thermodynamics. Each chapter gives a number of examples with detailed solutions in order to show how to apply the thermodynamic laws and formulas in solving concrete problems. Next, problems for independent work are given—the answers to which can be found at the end of the book.

The Appendices contain reference tables. They are needed, first, for solving the problems; and, second, they are of an independent significance because they will permit students to solve many thermodynamic problems proposed by the instructor or confronting them when studying special chemical subjects and chemical technology as well as when performing course or diploma work or designs. The Appendices are followed by a list of monographs and reference books that can be used in solving problems in chemical thermodynamics.

The present collection of examples and problems has been compiled using the experience gained through many years of teaching the course of chemical thermodynamics to students of the faculty of chemistry and chemical technology of the I. M. Gubkin Institute of the Petrochemical and Gas Industry in Moscow. It is based on up-to-date material published in recent years in monographs, reference books on physical chemistry and chemical thermodynamics, and in separate articles in various journals. Students study chemical thermodynamics after a course in physical chemistry. Although they are acquainted with the solution of some of the problems in the course of physical chemistry, our teaching experience has shown the great need for the proposed type of problem book, purposefully directed at training students in the methods of calculating chemical equilibria. The book will also be of interest for workers of research institutions and engineers specializing in chemistry and chemical technology.

Chapters 1 and 2 were compiled by V. A. Skoblo, and Chapters 3, 4 and 5 by A. S. Kazanskaya.

We express our deep gratitude to the late prof. V. A. Kireev, senior scientific worker A. A. Lopatkin, associate professor V. P. Dreving, and all of those in the department of physical chemistry of the Byelorussian State University headed by associate professor A. A. Vecher for their attentive critical analysis which helped us to improve the quality of the book.

G. M. Panchenkov

1

Calculation of the Heat

of a Chemical Reaction

Chemical processes are attended by the liberation or absorption of heat which is called the *heat of a reaction* (or the *heat effect* by some authors). A chemical reaction consists in the breaking of a definite number of chemical bonds between the atoms in a molecule and in the formation of new bonds. If the energy liberated in the formation of the new bonds exceeds that spent for breaking the bonds in the initial molecules, the reaction is attended by the liberation of heat (an *exothermic process*); if the energy liberated in the formation of the new bonds is less than that of breaking the bonds, the reaction is attended by the absorption of heat from the surroundings (an *endothermic process*). Consequently, in chemical transformations, the internal energy of the reacting molecules changes.

The change in the internal energy dU in the course of a chemical transformation occurs, according to the first law of thermodynamics, at the expense of the absorption (or liberation) of the heat δQ and the performance of the work δW. We shall write the analytical expression of the first law of thermodynamics in the form

$$dU = \delta Q - \delta W \qquad (1.1)$$

The change in the internal energy as a result of a chemical reaction does not depend on the path followed by it, but depends only on the initial and final states of the system.

The heat of a reaction in the general case is not a change in a function of state and, therefore, depends on the path of a process. In two very simple cases, however, when a process occurs at a constant pressure p or a constant volume V, the independence of the path also extends to the heat of the process (including a chemical reaction). If a reaction proceeds at $V = $ const, and no electrical or other kinds of work is performed, i.e. $W = 0$, then according to Eq. (1.1), with the temperature T constant, the heat of a reaction is

$$Q_V = U_2 - U_1 = \Delta U \qquad (1.2)$$

The heat of a chemical reaction Q_V (the subscript V denotes that $V = $ const) equals the change in the internal energy as a result of

the reaction. If a reaction proceeds at constant pressure and only the work of volume expansion is performed (other kinds of work are absent), the analytical expression of the first law of thermodynamics will become

$$\delta Q = dU + p\, dV \tag{1.3}$$

where the elementary work δW is represented only by the work of expansion, i.e. $\delta W = p\, dV$. Integration of Eq. (1.3) with $p = $ = const yields

$$Q_p = U_2 - U_1 + p\,(V_2 - V_1)$$

or

$$Q_p = (U_2 + pV_2) - (U_1 + pV_1) \tag{1.4}$$

Since p and V are parameters of state, while U is a function of state, the sum $(U + pV)$ is also a function of state. Its change does not depend on the path of a process, but only depends on the initial and final states of the participants of a reaction. This function is called *enthalpy* and is designated by the symbol H:

$$U + pV = H \tag{1.5}$$

Consequently

$$Q_p = H_2 - H_1 = \Delta H \tag{1.6}$$

If a reaction proceeds at constant pressure, then when $T = $ const, its heat equals the change in enthalpy as a result of the reaction.

Thus, in the above cases (1.2) and (1.6), the heat of a chemical process equals the change in the functions of state; therefore, it does not depend on the path of a process, but only depends on the initial and final states.

At present, customary practice is to write the heat of a reaction as follows. The stoichiometric equation of a reaction is attended by indication of the difference between the internal energies (or enthalpies) of the products and the reactants, i.e. $\Delta U = Q_V$ (or $\Delta H = $ = Q_p)—the growth in internal energy (or enthalpy). If this growth is positive, the reaction proceeds with the absorption of heat; and if it is negative, heat is liberated. For example, the oxidation of liquid benzene at constant pressure to carbon dioxide and liquid water proceeding with the liberation of heat is written as follows:

$$C_6H_6(lq) + \frac{15}{2}\,O_2(g) = 6CO_2(g) + 3H_2O(lq)$$
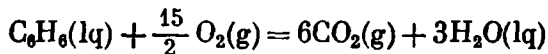
$$Q_p = \Delta H = -780\,980 \text{ cal}$$

The symbols (c), (lq), and (g) are used after the chemical formula of a substance to indicate whether it is crystalline (solid), liquid, or gaseous, respectively. These symbols are usually omitted when the state of aggregation of the components of a reaction is obvious. For instance, the hydrogenation of acetylene to ethane conducted at

constant pressure and at 25 °C proceeds in the gaseous phase. It may therefore be written as follows:

$$C_2H_2 + 2H_2 = C_2H_6, \quad Q_p = \Delta H = -74\ 430 \text{ cal}$$
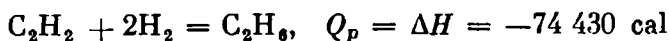
This reaction, like that in the preceding example, is exothermic.

The need to indicate the state of aggregation of reaction components is due to the fact that the heat of a reaction depends on the state of aggregation of the reactants and products. If the state of aggregation changes as a result of a chemical reaction, its heat also includes the heat of the relevant phase transition (heat of vaporization or condensation, fusion or freezing, sublimation or condensation).

The heat of a reaction depends on whether or not the temperature of the reactants and products is the same. If the products of a reaction proceeding with the liberation of heat have a higher temperature than the reactants, part of the liberated heat will go for heating the reactants. Consequently, the measured heat of the reaction will be less than when the temperature of the reactants and products is the same.

Therefore, when measuring the heat of a reaction, the temperature of the reactants must exactly equal that of the products.

For the convenience of further thermodynamic calculations, we shall denote the heat of a chemical reaction in conditions of constant pressure by the symbol ΔH, and in conditions of constant volume by the symbol ΔU. In laboratory and industrial conditions, we most often encounter reactions proceeding at constant pressure.

If ΔH is positive, the reaction, as noted above, is endothermic. For example for the thermal cracking of gas oils $\Delta H = +70$-250 kcal/kg of converted starting material; for the pyrolysis of kerosenes $\Delta H = +400$-500 kcal/kg; for platforming $\Delta H = +180$ kcal/kg; and for the catalytic cracking of petroleum fractions $\Delta H = +50$-1.30 kcal/kg.

If ΔH is negative, the process is exothermic. For example for the regeneration of the catalysts of catalytic cracking $\Delta H = -8000$ kcal/kg; for the hydrogenation of isooctene $\Delta H = -245$ kcal/kg; and for the alkylation of isobutane with isobutene $\Delta H = -250$ kcal/kg.

In previous publications, the thermochemical heats were used. They are denoted by the symbols $\bar{Q}_V$ and $\bar{Q}_p$ and differ from the thermodynamic heats described above (which we shall use in the following) in their sign:

$$Q = -\bar{Q}$$

This must be taken into consideration in reading chemical literature.

In the thermochemical writing of chemical reactions, the right-hand side of a reaction is followed by a term characterizing the

liberation or absorption of heat as its result. Equations written in this way are called *thermochemical*. The exothermic reactions considered above have the form

$$C_6H_6(lq) + \frac{15}{2} O_2(g) = 6CO_2(g) + 3H_2O(lq) + 780\,980 \text{ cal}$$

$$C_2H_2 + 2H_2 = C_2H_6 + 74\,430 \text{ cal}$$
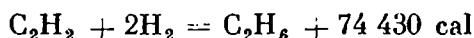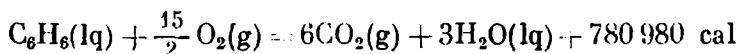
The endothermic reaction of formation of acetylene is written as follows:

$$2C(c) + H_2(g) = C_2H_2(g) - 54\,190 \text{ cal}$$

It is essential for thermochemical calculations that all the heats of reactions be related to identical conditions; otherwise their values will be incompatible. This is due to the fact that the heat of a chemical reaction depends on temperature and to a smaller extent on pressure. The heats of chemical reactions are customarily reduced to standard conditions. For individual solids and liquids, their state at 1 atm and the given temperature is taken as the standard one. For individual gases, their state in the form of a hypothetic ideal gas whose fugacity equals unity at the given temperature is taken as the standard one. The properties of individual gases at 1 atm do not differ too much from their properties in standard conditions; this difference is usually disregarded in calculations not requiring a high accuracy. Attention must be given to the circumstance that for a gaseous chemical reaction conducted in standard conditions it is not the total pressure that equals 1 atm, but the partial pressure of each of the gaseous reagents.

The heat of a chemical reaction conducted in standard conditions is designated ΔH_T°. The superscript indicates the standard state while the subscript is the temperature (in kelvins) at which the reaction is conducted. The standard heat of a reaction can be calculated for any temperature T, but most often 298.15 K (25.00 °C) is used. In this case, the standard heat of a reaction is denoted by ΔH_{298}°. The temperature 298.15 K is chosen because other very important characteristics of processes are given for this temperature. Calorimetric measurements are also related to it.

1.1
Relationship Between Heats of Reactions Proceeding at Constant Pressure (ΔH) and Constant Volume (ΔU)

In a chemical reaction, a change in the number of moles of one component unambiguously determines the change in the number of moles of the remaining components. We can therefore say that for

systems in which a reaction occurs the internal energy will be a function not only of temperature and volume, but also of the number of moles n of one of the reagents:

$$U = f(V, T, n) \tag{1.7}$$

The total differential of the internal energy

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V, n} dT + \left(\frac{\partial U}{\partial V}\right)_{T, n} dV + \left(\frac{\partial U}{\partial n}\right)_{V, T} dn \tag{1.8}$$

If we consider a system at $T = $ const and $p = $ const, then Eq. (1.8) may be rewritten in the form

$$\left(\frac{\partial U}{\partial n}\right)_{p, T} = \left(\frac{\partial U}{\partial V}\right)_{T, n} \left(\frac{\partial V}{\partial n}\right)_{p, T} + \left(\frac{\partial U}{\partial n}\right)_{V, T} \tag{1.9}$$

Differentiation of Eq. (1.5) yields

$$\left(\frac{\partial H}{\partial n}\right)_{p, T} = \left(\frac{\partial U}{\partial n}\right)_{p, T} + p\left(\frac{\partial V}{\partial n}\right)_{p, T} \tag{1.10}$$

Using Eq. (1.9) in (1.10), we get

$$\left(\frac{\partial H}{\partial n}\right)_{p, T} = \left(\frac{\partial U}{\partial n}\right)_{V, T} + \left[\left(\frac{\partial U}{\partial V}\right)_{T, n} + p\right]\left(\frac{\partial V}{\partial n}\right)_{p, T} \tag{1.11}$$

For the change in volume upon the conversion of one mole, we can write

$$\Delta V = \left(\frac{\partial V}{\partial n}\right)_{p, T} \tag{1.12}$$

But at $V = $ const, we have

$$dQ_V = (dU)_{V, T} = \left(\frac{\partial U}{\partial n}\right)_{V, T} dn \tag{1.13}$$

or

$$Q_V = (\Delta U)_{V, T} = \left(\frac{\partial U}{\partial n}\right)_{V, T} \Delta n \tag{1.14}$$

If $\Delta n = 1$, then

$$Q_V = \left(\frac{\partial U}{\partial n}\right)_{V, T} \tag{1.15}$$

We can prove by similar reasoning that

$$Q_p = \left(\frac{\partial H}{\partial n}\right)_{p, T} \tag{1.16}$$

Introducing Eqs. (1.12), (1.15), and (1.16) into Eq. (1.11), we get

$$Q_p = Q_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\Delta V \tag{1.17}$$

or

$$\Delta H = \Delta U + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\Delta V \tag{1.18}$$

If a reaction proceeds in a condensed phase (solids or liquids participate in it), the quantity ΔV is insignificant, and we may consider that $\Delta H = \Delta U$. If in a chemical reaction being studied, gaseous substances are formed or disappear at a low pressure, the resultant change in volume at $p = $ const and $T = $ const is significant. In this case, the quantity ΔV is determined from the equation of state of ideal gases:

$$\Delta V = \Delta n_g \frac{RT}{p} \tag{1.19}$$

where Δn_g is the growth in the number of moles of the gaseous reagents in accordance with the stoichiometric equation of the reaction.

Using Eq. (1.19) in (1.18) and taking into account that for ideal gases $(\partial U / \partial V)_T = 0$, we get

$$\Delta H = \Delta U + p \ \Delta V \tag{1.20}$$

or

$$\Delta H = \Delta U + \Delta n_g RT \tag{1.21}$$

Thus, the heat of a reaction ΔH at constant pressure differs from the heat of a reaction ΔU at constant volume by the amount of work done at the expense of a change in the number of moles of the reagents.

If an endothermic reaction is attended by a decrease in the number of moles of the gaseous reagents, the work done will be that of compression, and $\Delta H < \Delta U$. For an exothermic reaction in this case, we have $\Delta H > \Delta U$. If a reaction is attended by an increase in volume ($p \ \Delta V > 0$), then for an endothermic reaction we have $\Delta H > \Delta U$, and for an exothermic one $\Delta H < \Delta U$. And only in the special case when a gaseous reaction proceeds without any change in the number of moles, i.e. when $\Delta V = 0$, do we have $\Delta H = \Delta U$.

Example 1. According to Eq. (1.20), the relationship between the heats of a chemical reaction at $p = $ const and $V = $ const is given as $\Delta H = \Delta U + p \ \Delta V$. Give examples of reactions in the gaseous phase for which (1) $\Delta H > \Delta U$; (2) $\Delta H < \Delta U$; and (3) $\Delta H = \Delta U$.

Solution. It follows from Eq. (1.20) that the relationship between ΔH and ΔU is affected by the sign of the change in volume ΔV as a result of a reaction. Let us consider the endothermic reaction of decomposition of ammonia

$$2NH_3(g) = 3H_2(g) + N_2(g)$$

As a result of this reaction, the difference between the volume of the products (pr) and the reactants (r) is

$$\Delta V = V_{pr} - V_r = (3 + 1) - 2 = +2$$

which indicates expansion of the system. In this case, $\Delta H > \Delta U$.

For the exothermic reaction of formation of water from simple substances

$$2H_2(g) + O_2(g) = 2H_2O(g)$$
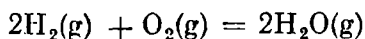
the change in volume $\Delta V = 2 - (2 + 1) = -1$. Hence, the reaction proceeds with compression of the system, and, therefore, $\Delta H <$ $< \Delta U$.

If a reaction proceeds without a change in volume ($\Delta V = 0$), for example the endothermic reaction of formation of hydrogen iodide

$$H_2(g) + I_2(g) = 2HI(g)$$
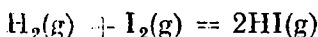
then $\Delta H = \Delta U$.

Example 2. The heat of the reaction of incomplete oxidation of carbon at constant volume $\Delta U = -26\,103$ cal at 25 °C. Calculate the heat of the reaction ΔH for the same temperature, but at constant pressure.

Solution. The relationship between the heats of a reaction at $p = $ const and $V = $ const is expressed by Eq. (1.20):

$$\Delta H = \Delta U + p\,\Delta V$$

We assume that the gaseous reagents in the reaction

$$C + \frac{1}{2}O_2\,(g) = CO(g)$$
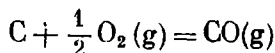
obey the laws of the ideal state. Hence, according to the Clapeyron-Mendeleev equation

$$p\,\Delta V = \Delta n_g RT$$

where Δn_g is the change in the number of moles of the gaseous reagents as a result of the reaction:

$$\Delta n_g = n_{g,2} - n_{g,1} = 1 - 0.5 = 0.5$$

Thus

$$\Delta H = \Delta U + \Delta n_g RT$$
$$\Delta H = -26\,103 + 0.5 \times 1.987 \times 298.15 =$$
$$= -26\,103 + 296 = -25\,807 \text{ cal}$$

Example 3. Find the difference between the heats $(\Delta H - \Delta U)$ for the reaction of thermal cracking of *n*-dodecane proceeding in the gaseous phase at atmospheric pressure and at 800 K.

Solution. The equation of the reaction is

$$C_{12}H_{26}(g) = C_6H_{12}(g) + C_4H_8(g) + C_2H_6(g)$$
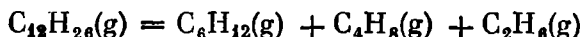
The change in the number of moles as a result of the reaction is

$$\Delta n_g = (1 + 1 + 1) - 1 = 2$$

Considering the reagents to be ideal gases, we use Eq. (1.21) to determine the difference $(\Delta H - \Delta U)$:

$$\Delta H - \Delta U = 2 \times 1.987 \times 800 = 3180 \text{ cal}$$

Example 4. Show that in the analytical expression of the first law of thermodynamics δQ is not a total differential (a function of state).

Solution. To prove this fact, we shall use the equation

$$\delta Q = dU + p\, dV$$

We assume that $U = f(V, T)$. Hence,

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

Inserting this value of the total differential into the initial equation, we get

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

Let us remember the property of a total differential. If z is a function of two variables x and y, i.e. $z = f(x, y)$, the equation

$$dz = M\, dx + N\, dy$$

(in which M and N are also functions of x and y) is a total differential on condition that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

It follows from this property of a total differential that if δQ were a total differential, then

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right], \quad \text{or} \quad \left(\frac{\partial p}{\partial T}\right)_V = 0$$

which is absurd in the general case.

1.2
Calculation of the Heats of Reactions. Hess's Law

It was shown above that $Q_p = \Delta H$ and $Q_V = \Delta U$. Since the internal energy U and enthalpy H are thermodynamic functions, i.e. functions of state, their change does not depend on the path followed by a system in transferring from one state to another,

but depends only on the initial and final states of the system. Consequently, the heats of reactions ΔH and ΔU also do not depend on the path along which a reaction proceeds, but depend only on the initial and final states of the reagents. This statement, which is a direct corollary of the first law of thermodynamics, is called *Hess's law*.

It follows from this law that:

1. The heat of formation of a compound from the initial substances does not depend on how this compound was obtained.

2. The heat of decomposition of a compound into the initial substances is equal and opposite in sign to the heat of formation of the compound from these initial substances.

3. If identical products are formed from two different systems as a result of different processes, the difference between the heats of these processes equals the heat of transformation of the first system into the second; if a transition occurs from identical initial states to different final ones, the difference between the heats of the processes equals the heat of transformation of one set of products into the other.

The great significance of Hess's law consists in that it can be used to calculate an unknown heat of a reaction by combining the stoichiometric equations and heats of other reactions that have been studied thermochemically. It is necessary only to compare the heats of different reactions for the same conditions.

Hess's law is indispensable for calculating the heats of reactions that cannot be measured by calorimetric means. For example the product of the reaction $C + O_2$ is CO_2, but upon incomplete combustion CO and CO_2 are formed. Owing to the reaction proceeding in two directions, it is impossible to directly determine the heat of formation of CO.

Another example of the application of Hess's law is a reaction of formation of hydrocarbons from simple substances, for instance

$$C + 2H_2 = CH_4$$

The heat of formation of methane cannot be measured directly, but it can be calculated on the basis of Hess's law.

Hess's law permits us to calculate the heat of any chemical reaction in one of the following ways: (1) by combining the equations of reactions; (2) with the aid of the heats of combustion of the substances participating in a reaction; and (3) using the heats of formation of the substances participating in a reaction. We shall consider each of these ways separately.

1.2.1. Determining Reaction Heats by Combining Equations of Reactions. We first determine what algebraic operations must be performed to get the required equation from those given for solving

a problem. We next perform similar algebraic operations with the heats of the corresponding reactions to find the required value.

If when determining the heat of a reaction it is necessary to use equations of many auxiliary reactions, the operations with the equations should not be selected mechanically, but the process should be mentally conducted through the reactions given for solving the problem posed. In other words, the reactants should be converted by means of some of the auxiliary reactions into intermediates which are then transformed into the products by means of the unused reactions. The question of whether or not the intermediate reactions can actually be carried out is naturally of no significance whatsoever in the given case.

Example 5. Knowing the heats of the reactions

(1) C (graphite) $+ O_2(g) = CO_2(g)$, $\Delta H^{(1)} = -94\,052$ cal

(2) $CO(g) + \frac{1}{2} O_2(g) = CO_2(g)$, $\Delta H^{(2)} = -67\,636$ cal

(3) $H_2(g) + \frac{1}{2} O_2(g) = H_2O(g)$, $\Delta H^{(3)} = -57\,798$ cal

determine the heats of the following reactions:

(4) C (graphite) $+ \frac{1}{2} O_2(g) = CO(g)$, $\Delta H^{(4)} = ?$

(5) C (graphite) $+ H_2O(g) = CO(g) + H_2(g)$, $\Delta H^{(5)} = ?$

(6) C (graphite) $+ 2H_2O(g) = CO_2(g) + 2H_2(g)$, $\Delta H^{(6)} = ?$
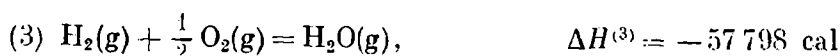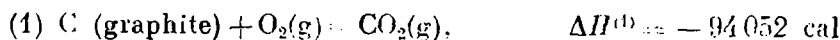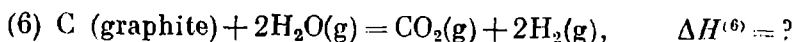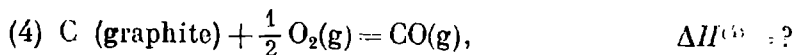
Solution. Subtracting the second equation from the first, we get

$$C \text{ (graphite)} + \frac{1}{2} O_2(g) = CO(g)$$
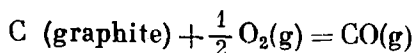
whence

$$\Delta H^{(4)} = \Delta H^{(1)} - \Delta H^{(2)} = -94\,052 + 67\,636 = -26\,416 \text{ cal}$$

Subtracting the third equation from the fourth, we have

$$C \text{ (graphite)} - H_2(g) = CO(g) - H_2O(g)$$

or

$$C \text{ (graphite)} + H_2O(g) = CO(g) + H_2(g)$$
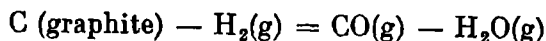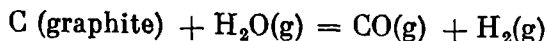
$$\Delta H^{(5)} = \Delta H^{(4)} - \Delta H^{(3)} = -26\,416 + 57\,798 = +31\,382 \text{ cal}$$

Finally, multiplying the third equation by two, we get

$$2H_2(g) + O_2(g) = 2H_2O(g)$$
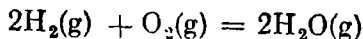
We subtract the equation obtained from the first one:

$$C \text{ (graphite)} + 2H_2O(g) = CO_2(g) + 2H_2(g)$$
$$\Delta H^{(6)} = \Delta H^{(1)} - 2\,[\Delta H^{(3)}] = -94\ 052 - 2\,(-57\ 798) =$$
$$= +21\ 544 \text{ cal}$$
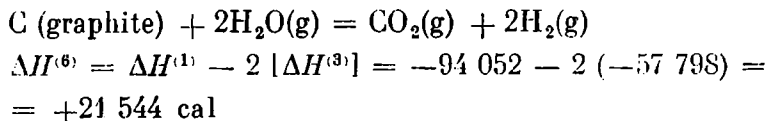
In the above example, the first four reactions are exothermic, the last two are endothermic.

Example 6. Using the following data:

(1) $4NH_3 + 3O_2 = 2N_2 + 6H_2O$, $\Delta H = -362\ 400$ cal

(2) $2H_2 + O_2 = 2H_2O$, $\Delta H = -136\ 800$ cal

(3) $NH_3 + aq = NH_3 \cdot aq$, $\Delta H = -8400$ cal
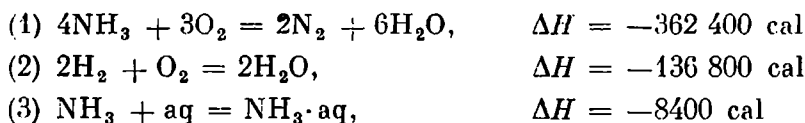
calculate the heat of formation of ammonia from its aqueous solution.

Solution. We multiply the first equation by $-\dfrac{1}{4}$, the second by $+\dfrac{3}{4}$ and add them:

(4) $\dfrac{1}{2}N_2 + \dfrac{3}{2}H_2 = NH_3$, $\Delta H = -12\ 000$ cal
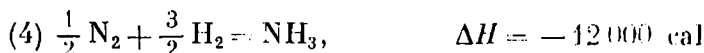
We add the fourth and third equations:

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 + aq = NH_3 \cdot aq, \qquad \Delta H = -4600 \text{ cal}$$
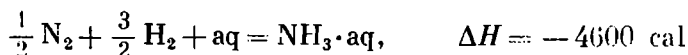
Example 7. Calculate the heat of the reaction

$$NH_3(g) + \frac{5}{4}O_2(g) = NO(g) + \frac{3}{2}H_2O(g)$$

using the following data:

$$H_2O(g) = H_2O(lq), \qquad \Delta H^{(1)} = -10\ 520 \text{ cal}$$

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(g), \qquad \Delta H^{(2)} = -11\ 040 \text{ cal}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(lq), \qquad \Delta H^{(3)} = -68\ 320 \text{ cal}$$

$$NO(g) = \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g), \qquad \Delta H^{(4)} = -21\ 600 \text{ cal}$$
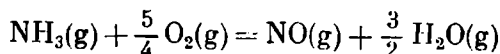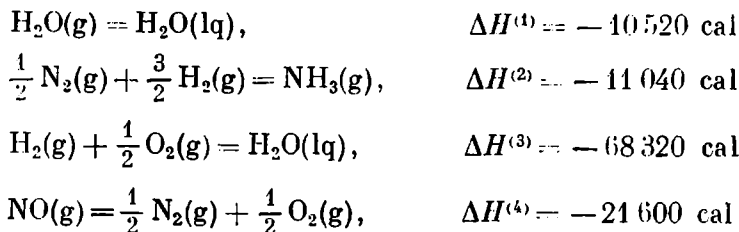
Solution. We mentally imagine the reaction of direct oxidation of ammonia to proceed as follows. The ammonia decomposes into nitrogen and hydrogen; next the nitrogen and part of the oxygen form nitric oxide, while the hydrogen combines with the remaining oxygen to form water, which transforms into the vapour. Since the sum of these reactions is equivalent to the basic reaction, by equat-

ng their heats we get

$$\Delta H = -\Delta H^{(2)} - \Delta H^{(4)} + \frac{3}{2} \Delta H^{(3)} - \frac{3}{2} \Delta H^{(1)} = -54\,060 \text{ cal}$$

1.2.2. Calculating the Heat of Reactions from the Heats of Combustion of the Substances Participating in Them. It follows from Hess's law that the heat of a reaction equals the sum of the heats of combustion of the reactants minus the sum of the heats of combustion of the products:

$$\Delta H = \sum (\nu_i \Delta H_{\text{comb}, i})_r - \sum (\nu'_i \Delta H_{\text{comb}, i})_{pr} \qquad (1.22)$$

where ν_i and ν'_i are the stoichiometric coefficients of the reactants and products, respectively.

By the *heat of combustion* is meant the heat of the reaction of oxidation of a given compound by oxygen with the formation of the higher oxides of the relevant elements. The heat of combustion is customarily related to one mole of a reactant.

It is possible to directly determine the heats of combustion for organic compounds. It is quite easy to burn any hydrocarbon, alcohol, ether, ester, and other individual substances to obtain CO_2 and liquid H_2O. On the other hand, it is impossible in the majority of cases to obtain a given individual compound from simple substances by their direct reaction without speaking of the difficulties encountered in measuring the heat of such a process. This is why the calculation of the heats of reactions according to the heats of combustion of the substances participating in them has come into great favour for organic reactions.

For thermochemical calculations, all the heats must be related to identical conditions—isobaric or isochoric. Since isobaric processes are more frequently encountered in chemistry and chemical technology, publications on the subject generally give the isobaric heats of combustion, designated by the symbol ΔH_{comb}.

For convenience in comparing experimental data and subsequent calculations, the experimental heats of combustion of substances are usually related to standard conditions, i.e. to a process in which both the reactants and the products are in a standard (thermodynamically stable at a given temperature) state at a pressure of 1 atm. As regards the temperature, in the overwhelming majority of the late thermochemical papers, publications and reference books, the heats of combustion are related to 25 °C (298.15 K). The heat of combustion related to standard conditions at 298.15 K (25 °C) is designated by the symbol $(\Delta H^{\circ}_{298})_{\text{comb}}$. The standard heats of combustion of various substances at 25 °C can be found in reference books and special publications [1-12]. The values of $(\Delta H^{\circ}_{298})_{\text{comb}}$ for selected substances are also given in the present book (Appendix 1).

A substance is usually burnt isothermally in a calorimetric bomb at constant volume in an atmosphere of pure oxygen and a pressure of 20 to 30 atm. Consequently, the value obtained as a result of an experiment is the heat of combustion at $V = $ const: $Q_V = \Delta U$. And since the combustion of organic substances is attended by diminishing of their internal energy, the change in the latter as a result of the reaction of combustion will always be negative $(-\Delta U)$.

We use the symbol ΔU° to denote the change in the internal energy of combustion of a substance in standard conditions, i.e. when the partial pressures of the reactants (the substance being burnt and oxygen) and the products [$CO_2(g)$ and $H_2O(lq)$] equal 1 atm at 25 °C. It should be noted that the difference between the quantities ΔU and ΔU° is often appreciable.

E. Washburn [13] considered all the thermodynamic conditions of the combustion process for a substance having the composition $C_a H_b O_c$ conducted in a calorimetric bomb and gave detailed recommendations on how to convert ΔU to ΔU°. According to Washburn, this can be done as follows. Since the change in internal energy does not depend on the path of a process and is unambiguously determined only by the initial and final states of a system, let us consider how these states differ for a real process proceeding in a bomb and for the same process in standard conditions.

The following diagram will help us explain the essence of the matter:
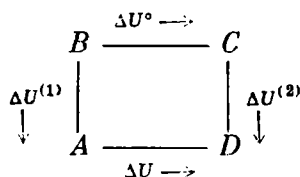
Points B and C denote the initial and final states in the process of combustion of a mole of a given substance in standard conditions at 25 °C. Thus, the quantity ΔU° is the standard change in internal energy in the process of complete combustion of the substance being studied. Points A and D denote the initial and final states of combustion of a mole of a given substance in the bomb. ΔU is the change in the internal energy in the process occurring in the bomb.

Inspection of the diagram shows that to calculate ΔU° and ΔU we must know $\Delta U^{(1)}$ and $\Delta U^{(2)}$. Let us write the following equations, in which U with the corresponding superscript stands for the internal energy of the system in a given state:

$$\Delta U^\circ = U^{(c)} - U^{(b)}, \qquad \Delta U^{(2)} = U^{(d)} - U^{(c)}$$

$$\Delta U = U^{(d)} - U^{(a)}, \qquad \Delta U^{(1)} = U^{(a)} - U^{(b)}$$

On the basis of these equations we have

$$\Delta U^\circ + \Delta U^{(2)} = \Delta U^{(1)} + \Delta U$$

or

$$\Delta U^\circ = \Delta U - \Delta U^{(2)} + \Delta U^{(1)}$$

Thus, to calculate ΔU° we must add the change in the internal energy $\Delta U^{(1)}$ connected with the process of transition of the reactants from their standard state to the final one in the bomb to the quantity ΔU and subtract $\Delta U^{(2)}$—the change in the internal energy connected with the process of transition of the products from their standard state to the initial one in the bomb.

Washburn considered procedures for calculating the changes in the internal energy $\Delta U^{(1)}$ and $\Delta U^{(2)}$. He recommended, an approximate formula to be used in converting ΔU to ΔU° for substances having the composition $C_a H_b O_c$. The deviation of ΔU and ΔU° expressed in per cent of the found value of ΔU is

$$\pi = \frac{0.30 pa}{\Delta U} \left[-1 + 1.1 \left(\frac{b - 2c}{4a} \right) - \frac{2}{p} \right] \qquad (1.23)$$

where p = initial pressure of the oxygen in the bomb, atm

$\Delta U/a$ = heat of combustion of the carbon contained in the substance being burnt, kcal/g·atom

a, b, c = subscripts in the chemical formula of the substance being burnt.

The correction (in per cent of ΔU) calculated by this equation has to be added to ΔU to obtain the required value of ΔU°.

A similar expression for the correction is recommended by O. Prosen [14] for compounds having the composition $C_a H_b O_c N_d$.

Since the introduction of Washburn's correction gives us ΔU°— the change in the internal energy for the process of combustion in standard conditions at V = const, it will no longer be difficult to calculate the standard heat of combustion ΔH°_{comb} for this process.

Upon the complete combustion of an organic substance, the carbon transforms into CO_2, the hydrogen into water, the sulphur into SO_2, while other substances, for example nitrogen, are liberated in the free state. The heat of combustion may have different values (higher and lower) depending on whether the water among the combustion products is in the liquid or the gaseous state.

At constant volume, the reaction of combustion of an organic substance having the composition $C_a H_b O_c N_d$ is expressed by the equation

$$C_a H_b O_c N_d (lq) + \left(a + \frac{b}{4} - \frac{c}{2} \right) O_2 =$$

$$= a CO_2 + \frac{b}{2} H_2 O (lq) + \frac{d}{2} N_2, \quad \Delta U^\circ$$
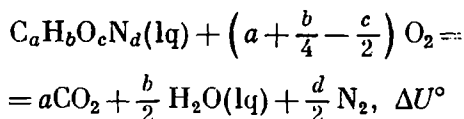
We can see that the reaction consumes $(a + b/4 - c/2)$ moles of gaseous oxygen while the combustion products contain $(a + d/2)$ moles of gaseous substances. Therefore, if combustion occurs at constant pressure, apart from the liberation of heat, positive or negative isothermal work will be done equal to

$$\left[\left(a + \frac{b}{4} - \frac{c}{2}\right) - \left(a + \frac{d}{2}\right)\right] RT = \frac{1}{2}\left(\frac{b}{2} - c - d\right) RT$$

The relationship between the heats at constant pressure and at constant volume, as noted on a previous page, is described by Eq. (1.21).

Taking $R = 2$ cal/mol·K, we obtain

$$\Delta H^\circ = \Delta U^\circ + T\left(\frac{b}{2} - c - d_i\right) \tag{1.24}$$

Equation (1.24) is used to convert the standard heat of combustion at constant volume ΔU°_{298} to the standard heat of combustion at constant pressure $(\Delta H^\circ_{298})_{comb}$.

The standard heats of combustion of substances in the gaseous state $(\Delta H^\circ_{298})^g_{comb}$ can be obtained from the standard heats of combustion of the substances in the liquid state $(\Delta H^\circ_{298})^{lq}_{comb}$ by adding to them the molar heat of vaporization of the relevant substance in the standard state at 25 °C.

The widespread use of the heats of combustion of organic compounds for calculating the heats of reactions with the aid of Eq. (1.22) is explained by two reasons. First, combustion in oxygen is a reaction common to all organic substances and proceeding, when certain conditions are observed, to the end, i.e. completely and unambiguously. Second, the technique of burning organic substances at constant volume is at a very high level and makes it possible to determine the heat of combustion with an accuracy up to $\pm 0.02\%$.

A great but inevitable shortcoming in calculating the heats of reactions with the aid of Eq. (1.22) is the lowering of the relative accuracy of the results obtained in comparison with the accuracy of the initial data. Apart from the summation of the errors made in measuring the heats of combustion of the reagents, the fact that the heat of the reaction between the reagents is almost always smaller (and generally much smaller) than the heats of combustion of the reagents also tells. The relative error in the heat of a reaction found by Eq. (1.22) often equals several per cent, while for reactions whose heat is not great, for example for reactions of isomerization, the error may reach many scores of per cent.

At present, data on the heats of combustion for compounds of some of the homologous series of hydrocarbons are available in especially great detail in publications on the subject [1, 3, 6, 9]. Thus, for alkanes having a normal structure and an iso-structure, the values of

$(\Delta H^{\circ}_{298})_{comb}$ can be found in [1, 3, 6]. Excellent data are given for a number of primary aliphatic alcohols of normal structure and monocarboxylic acids in [1, 2]. The heats of combustion of alkyl-substituted benzoic acids are given in [4]. The data on the heats of combustion of ethers have been widened [1, 2]. A comparatively large amount of information is available on organic compounds containing sulphur [10], chlorine [15], bromine, etc.

A good review of publications on the heats of combustion of oxygen-containing organic compounds is contained in [11]. Recently a review devoted to the thermochemistry of nitrocompounds was published [16]. For most of the remaining classes of organic compounds, only a small amount of fragmentary data is available in the best case, while for very many series of even comparatively simple organic hydrocarbons, we have to note the complete absence of reliable thermochemical data.

Example 8. Determine the standard heat of the reaction of formation of benzene from acetylene at 25 °C if we know the standard heats of combustion of the substances participating in the reaction at the same temperature:

$$3C_2H_2(g) = C_6H_6(lq)$$
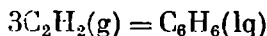
$(\Delta H^{\circ}_{298})_{comb}$, kcal/mol   — 310.62   — 781.00*

Solution. By Eq. (1.22), the heat of the required reaction is

$$\Delta H^{\circ}_{298} = 3\,(-310.62) - (-781.00) = -150.86 \text{ kcal}$$

Example 9. Find the standard heat of the reaction of destructive hydrogenation (hydrocracking) of *n*-heptane at 25 °C if we know the standard heats of combustion of the reaction reagents (kcal/mol):

$$C_7H_{16}(g) + 3H_2(g) = C_2H_6(g) + 2CH_4(g) + C_3H_8(g)$$

$(\Delta H^{\circ}_{298})_{comb}$ — 1160.0 — 68.31 —   372.82 — 212.79   —   530.60

Solution. The standard heat of the reaction at 25 °C is

$$\Delta H^{\circ}_{298} = (-1160.0 - 3 \times 68.31) - (-372.82 -$$
$$- 2 \times 212.79 - 530.60) = -35.93 \text{ kcal}$$

Example 10. Calculate the standard heat of the reaction of dehydrogenation of ethane

$$2C_2H_6(g) = 2CH_4(g) + C_2H_2(g) + H_2(g)$$
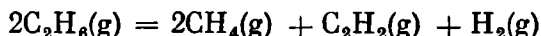
conducted in the gaseous phase at 298.15 K.

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* We shall use similar notation in all the following examples because we find it the most convenient. First the stoichiometric equation of a reaction is written, and the value needed for the solution is written under each of its participants. Then the symbol of the quantity and its unit are written to the left and below the reaction equation.

Solution. We use the corollary of Hess's law, i.e. Eq. (1.22). We find the heats of combustion of the substances participating in the reaction from Appendix 1:

$$2C_2H_6(g) = 2CH_4(g) + C_2H_2(g) + H_2(g)$$

$(\Delta H^\circ_{298})_{comb}$, kcal/mol -372.820 -212.800 -310.620 -68.310
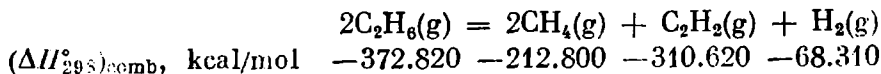
By Eq. (1.22), the standard heat of the reaction at 298.15 K is

$$\Delta H^\circ_{298} = 2\,(-372.820) + (2 \times 212.800 + 310.620 +$$
$$+ 68.310) = +58.89 \text{ kcal}$$

Example 11. When liquid tetrahydropyran $C_5H_{10}O$ was burnt in a calorimetric bomb at $V = $ const and 25 °C (the initial pressure of the oxygen was 30 atm), the heat of combustion obtained was $\Delta U = -749.63 \pm 0.12$ kcal/mol [12]. Calculate the standard heat of combustion of the above compound in the liquid state at 25 °C.

Solution. We use Eq. (1.23) to calculate Washburn's correction π which allows us to convert the experimentally found value of ΔU to the standard value ΔU°. For $C_5H_{10}O$, we have $a = 5$, $b = 10$, and $c = 1$. Hence,

$$\pi = \frac{0.30 \times 30 \times 5}{-749.63}\left[-1 + 1.1\left(\frac{10 - 2 \times 1}{4 \times 5}\right) - \frac{2}{30}\right] = +0.038\,\%$$

The plus sign indicates that to obtain ΔU° the value of ΔU must be lowered by 0.04% (approximately):

$$\Delta U^\circ = \frac{-749.63 \times 99.96}{100} = -749.33 \text{ kcal/mol}$$

Now we calculate the standard heat of combustion $(\Delta H^\circ_{298})_{comb}$ at 25 °C. Combustion of liquid tetrahydropyran follows the equation

$$C_5H_{10}O(lq) + 7O_2(g) = 5CO_2(g) + 5H_2O(lq)$$
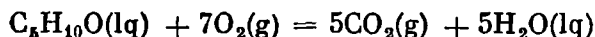
Therefore, seven moles of O_2 are used in the combustion of one mole of tetrahydropyran with the formation of five moles of gaseous CO_2; the change in the number of moles in the gaseous state will be

$$\sum n_g = 5 - 7 = -2$$

By Eq. (1.21) we have

$$(\Delta H^\circ_{298})_{comb} = \Delta U^\circ_{298} + \sum n_g RT$$
$$(\Delta H^\circ_{298})_{comb} = -749.33 - 2 \times 1.987 \times 10^{-3} \times 298.15 =$$
$$= -750.51 \text{ kcal/mol}$$

Since small corrections are calculated with sufficient accuracy, so as not to appreciably change the accuracy of measuring the basic

quantity, the error established for ΔU should be added to $(\Delta H^\circ_{295})_{comb}$. Thus, the standard heat of combustion of liquid tetrahydropyran is

$$(\Delta H^\circ_{298})^{iq}_{comb} = -750.51 \pm 0.12 \text{ kcal/mol}$$

1.2.3. Calculating the Heat of Reactions from the Heats of Formation of the Substances Participating in Them. Hess's law permits us to calculate the heats of many diverse reactions according to the minimum number of heats of some reactions. It was shown above that the heats of combustion can be chosen for this purpose. In thermochemical calculations, however, the heats of formation of chemical compounds from simple substances are generally used.

By the *heat of formation* of a compound is meant the heat of formation (usually at constant pressure) of one mole of the compound from the corresponding simple substances. It is considered here that the simple substances react in the form of the modification and the state of aggregation which correspond to their most stable state in the given conditions.

In a number of cases, reactions of formation of a compound from simple substances can be carried out, and the heat of formation can be measured directly. As a rule, however, the heats of formation of compounds are obtained mainly by calculations according to Hess's law from other thermochemical quantities.

When dealing with the heat of formation of a given compound, we must indicate exactly the substances (and their states) which it is formed from and the conditions for proceeding of the reaction we have in view. For example, we can speak of the heat of formation of H_2SO_4 from (a) H_2, O_2 and S; (b) H_2O and SO_3; and (c) SO_2, H_2 and O_2.

The heats of formation are often related to hypothetic reactions. For instance, the reaction of formation of potassium nitrate

$$K(c) + \frac{1}{2} N_2(g) + \frac{3}{2} O_2(g) = KNO_3(c)$$
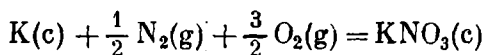
cannot be conducted, but this is of no significance for calculations because the heats of formation are only intermediate quantities in computing the heats of reactions. According to another corollary of Hess's law, the heat of any reaction equals the sum of the heats of formation of the products from simple substances minus the sum of the heats of formation of the reactants:

$$\Delta H = \sum (v'_i \Delta H_{form, i})_{pr} - \sum (v_i \Delta H_{form, i})_r \qquad (1.25)$$

To permit their comparison and use for calculations according to Hess's law, the heats of formation of chemical compounds are calculated for standard conditions. The heat of the reaction of formation of one mole of a given compound from simple substances in

standard conditions at a given temperature T is called the *standard heat of formation* and is denoted by the symbol $(\Delta H_T^\circ)_{form}$. The simple substances are taken in modifications that are thermodynamically stable at the given temperature. The reaction proceeds isothermally in standard conditions, and the product is obtained in its thermodynamically stable modification.

The standard heats of formation of a compound from simple substances are tabulated. The most complete list of values of the standard heats of formation at 25 °C, i.e. $(\Delta H_{298}^\circ)_{form}$, can be found in fundamental reference books [1-3, 5, 7-9, 16-35]. The values of $(\Delta H_{298}^\circ)_{form}$ for selected simple substances, inorganic, and organic compounds are given in Appendix 1 of the present book. Such tables often contain standard heats of formation of chemical compounds in states of aggregation that are not stable (and even impossible) in standard conditions. For example, the heat of formation from simple substances of water vapour in the hypothetic state of an ideal gas at 25 °C and a saturated vapour pressure equal to 1 atm is given $[(\Delta H_{298}^\circ)_{form}^g = -57\,798$ cal/mol]. The standard heat of formation of liquid water is $-68\,317$ cal/mol and differs from the corresponding value for the gaseous state by the standard molar heat of vaporization

$$-57\,798 - (-68\,317) = 10\,519 \quad \text{cal/mol}$$

The standard heats of formation of simple substances are obviously equal to zero.

The quantity $(\Delta H_{298}^\circ)_{form}$ is sometimes called the standard enthalpy of formation from simple substances.

It is sometimes interesting to determine the heat of formation of chemical compounds from atoms instead of from simple substances, i.e. from hypothetic monoatomic gases (the *atomic heat of formation*). The heat liberated (mentally) in this process is a measure of the energy of all the bonds and interaction between the atoms in a molecule and is of great significance for establishing the energy of each chemical bond. The heat of formation of compounds from simple substances should be distinguished from the atomic heat of formation. To calculate the latter, we must take into account the heat of sublimation of solid substances and the heat of dissociation of molecules of gaseous substances into atoms.

Whereas the heat of formation of any substance from atoms is negative (the formation of chemical bonds between atoms is always connected with the liberation of energy), the quantity $(\Delta H_{298}^\circ)_{form}$ may be either positive or negative. This depends on the balance of the energy of breaking the chemical bonds in simple substances and of the formation of new bonds in a given substance.

Example 12. Find the heat of the reaction of preparation of ethanol at $p =$ const and 25 °C if the standard heats of formation of the reagents from simple substances are known:

$$C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$$

$(\Delta H^\circ_{298})_{form}$, kcal/mol $+12.496$ -57.798 -56.240
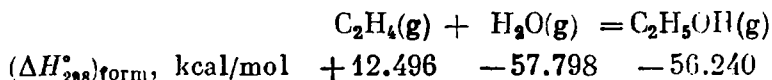
Solution. According to Eq. (1.26), the standard heat of the reaction is

$$\Delta H^\circ_{298} = -56.240 - (+12.496 - 57.798) = -10.938 \text{ kcal}$$

Example 13. Determine the standard heat of the reaction of preparation of 1,3-butadiene from ethanol proceeding in the gaseous phase at 25 °C. Use Appendix 1 in the calculations.
Solution. The formation of 1,3-butadiene from ethanol follows the equation

$$2C_2H_5OH(g) = C_4H_6(g) + H_2(g) + 2H_2O(g)$$
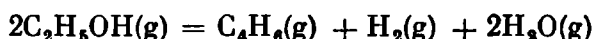
The standard heats of formation of the substances participating in the reaction from simple substances are -56.240, $+26.330$, 0, and -57.798 kcal/mol, respectively (Appendix 1). Hence,

$$\Delta H^\circ_{298} = (+26.330 + 0 - 2 \times 57.798) - (-2 \times 56.240) =$$

$$= +23.214 \text{ kcal}$$

Example 14. One of the methods of producing acetylene is the oxidizing pyrolysis of methane (incomplete combustion in oxygen). Calculate the standard heat of this reaction at 25 °C.
Solution. The reaction of oxidizing pyrolysis follows the equation

$$11CH_4(g) + 7O_2(g) = 2C_2H_2(g) + 6CO(g) + 14H_2(g) +$$

$$+ CO_2(g) + 6H_2O(g)$$
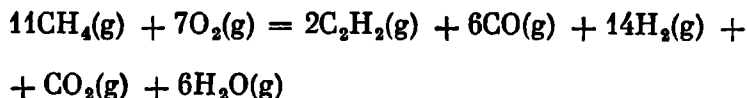
To solve the problem, we shall use the corollary of Hess's law in the form of Eq. (1.25). The standard heats of formation of the reagents from simple substances found in the tables of Appendix 1 are $(\Delta H^\circ_{298})_{form} = -17.889$, 0, $+54.194$, -26.416, 0, -94.052, and -57.798 kcal/mol, respectively. The required heat of the reaction is

$$\Delta H^\circ_{298} = (2 \times 54.194 - 6 \times 26.416 + 14 \times 0 - 94.052 -$$

$$- 6 \times 57.798) - (-11 \times 17.889 + 7 \times 0) = -294.169 \text{ kcal}$$

I.3
Empirical Methods for Determining the Standard Heats of Combustion and Formation of Organic Compounds from Simple Substances

We have shown in the preceding section that Hess's law and its corollaries make it a simple matter to calculate the heat of practically any reaction when data are available on the heats of combustion or formation of the reagents from simple substances. At present, the heats of combustion and formation of very many, but far from all, chemical compounds have been established experimentally. The number of experimental thermochemical studies are sharply growing from year to year, but the need for thermochemical data for new production processes and for solving other problems is growing at a still greater rate. It is therefore unreal to expect that the development of experimental work in the future will be able to completely satisfy the demand for thermochemical data, and it becomes necessary to place great hopes on methods of calculation. The latter make it possible, using a small stock of reliable data obtained experimentally, to calculate similar data for other compounds of the same class. Considerable success has been achieved at present in the development of such methods. Below is given a brief description of them.

We shall set out the most widespread approximate laws, often deprived of a theoretical substantiation and found by comparing a great amount of experimental data. Such empirical laws serve for the approximate calculation of $(\Delta H^{\circ}_{298})_{comb}$ and $(\Delta H^{\circ}_{298})_{form}$ at 25 °C when no experimental data are available.

The empirical methods of calculating the thermodynamic properties of organic substances are described in greater detail in a monograph by V. Kireev [17].

A. Methods of Calculating the Standard Heats of Combustion $(\Delta H^{\circ}_{298})_{comb}$ at 25 °C

1.3.1. Konovalov's Method of Calculating $(\Delta H^{\circ}_{298})_{comb}$. The approximate method proposed by D. Konovalov (1917) is a very simple one for calculating the standard heats of combustion of organic compounds in the gaseous state at 25 °C. He proposed to determine the standard heat of combustion of an organic compound to liquid water and carbon dioxide as follows:

$$(\Delta H^{\circ}_{298})_{comb} = -(48.8n + 10.6m + x) \text{ kcal/mol} \qquad (1.26)$$

$$(\Delta H^{\circ}_{298})_{comb} = -(204.2n + 44.4m + x) \text{ kJ/mol} \qquad (1.27)$$

where $n =$ number of moles of oxygen needed for the complete combustion of a substance

$m =$ number of moles of water formed

$x =$ correction quantity which Konovalov called the *thermal characteristic*.

For a compound $C_a H_b O_c$, we have $n = 2a + \frac{1}{2} b - c$ and $m = \frac{1}{2} b$. For all saturated organic compounds, $x = 0$. For unsaturated compounds, $x > 0$. The value of x is constant for all the compounds of a given homologous series and grows with the degree of unsaturation (Appendix 2).

The factor 48.8 in Eq. (1.26) expresses the heat of complete combustion of carbon reduced to one gramme-atom of oxygen, and the factor 10.6 the heat of condensation of the water vapour formed in combustion.

Example 15. Calculate the heating value of propane in standard conditions at 25 °C. Compare the results of the calculations with the tabulated value [3] of $(\Delta H^{\circ}_{298})_{comb} = -530.60$ kcal/mol.

Solution. The complete combustion of propane follows the equation

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O(lq)$$
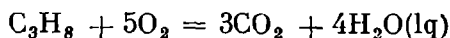
The quantities in Eq. (1.26) are $n = 10$, $m = 4$, and $x = 0$ (Appendix 2), respectively. Hence,

$$(\Delta H^{\circ}_{298})_{comb} = -(48.8 \times 10 + 10.6 \times 4) =$$

$$= -530.08 \text{ kcal/mol}$$

The results of the calculations differ from the tabulated value by 0.52 kcal/mol (0.098 %).

Example 16. Calculate $(\Delta H^{\circ}_{298})_{comb}$ for gaseous acetaldehyde. Compare the value obtained with the experimental one [1] $[(\Delta H^{\circ}_{298})_{comb} = -285$ kcal/mol].

Solution. The equation of the reaction of complete combustion of acetaldehyde is

$$CH_3COH + \frac{5}{2} O_2 = 2CO_2 + 2H_2O$$
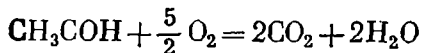
For this reaction, we have $x = 18$, $n = 5$, and $m = 2$. Hence,

$$(\Delta H^{\circ}_{298})_{comb} = -(48.8 \times 5 + 10.6 \times 2 + 18) =$$

$$= -283.2 \text{ kcal/mol}$$

The relative error of the calculations is 0.06 %.

Example 17. Calculate $(\Delta H_{298}^{\circ})_{comb}$ for gaseous cinnamic aldehyde $C_6H_5CH=CHCHO$.

Solution. The equation of the reaction of combustion is

$$C_6H_5(CH_2)CHO + \frac{21}{2} O_2 = 9CO_2 + 4H_2O$$
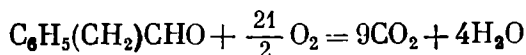
We have $n = 21$ and $m = 4$. The value of x is the sum of the relevant values for the phenyl group (24), the double bond (21), and the aldehyde group (18) (see Appendix 2). Hence,

$$(\Delta H_{298}^{\circ})_{comb} = -[48.8 \times 21 + 10.6 \times 4 + (24 + 21 + 18)] =$$
$$= -1130.2 \text{ kcal/mol}$$

According to published data [8], we have $(\Delta H_{298}^{\circ})_{comb} = -1130.0$ kcal/mol.

1.3.2. Kharasch's Method of Calculating $(\Delta H_{298}^{\circ})_{comb}^{lq}$. M. Kharasch [37] proposed a general method of calculating the standard heats of combustion at 25 °C for liquid organic compounds of various classes. Considering any organic compound as a hydrocarbon in which a certain number of hydrogen atoms are substituted by various atoms and groups, and considering $(\Delta H_{298}^{\circ})_{comb}$ to be a function of the number of electrons migrating upon combustion to the oxygen atoms, Kharasch obtained the following formula for calculations:

$$(\Delta H_{298}^{\circ})_{comb} = -26.050(4C + H - p) + \sum k_i \Delta_i \text{ kcal/mol} \quad (1.28)$$

where -26.050 = heat of breaking of the bonds C—C, C—H and the following formation of CO_2 and H_2O, kcal/mol·electron

$\quad\quad\quad$ C = number of carbon atoms in the compound

$\quad\quad\quad$ H = number of hydrogen atoms in the compound

$\quad\quad\quad$ p = number of partially displaced electrons in a molecule of the compound

$\quad\quad\quad$ k_i = number of identical substituents

$\quad\quad\quad$ Δ_i = heat correction corresponding to a given substituent.

Calculations according to Eq. (1.28) are based on a number of assumptions: (1) upon combustion the valence electrons migrate from the atoms of the organic compound to those of oxygen; (2) four electrons migrate from each carbon atom, and one electron from each hydrogen atom; and (3) if hydrogen in a compound is substituted by another atom or group of atoms, the electronic structure of the molecule will change, and the heat of combustion of the compound will increase or diminish by the magnitude of the structural correction Δ_i; the number of electrons migrating to the oxygen will diminish by the quantity p equalling the number of electrons

having a strong bond to the atoms substituting the hydrogen atoms in the compound.

Electrons can be partially displaced in a molecule of a compound only by atoms of strong oxidizers (oxygen, halogens, etc.), the number of such partially displaced electrons usually corresponding to the valence of an atom of the oxidizer in the given molecule. For example in C_6H_6 we have $p = 0$, in C_2H_5OH we have $p = 2$, in C_6H_5Cl we have $p = 1$, etc. The values of the heat corrections Δ_i for Eq. (1.28) and the number of partially displaced electrons for various groups and substituents are given in Appendix 3.

Kharasch's method is very approximate, and it permits us to assess the value of $(\Delta H^\circ_{298})_{comb}$ very roughly. It should be resorted to in the complete absence of experimental data.

The laws established by Kharasch can be presented in a more convenient form. A. Frost [3] expressed the dependence of the heat of combustion on the size of a molecule of a compound, taking into account the number of carbon and hydrogen atoms in it, whereas Kharasch took the number of valence electrons in a molecule as the independent variable. As a result, Frost obtained the following equation allowing us to calculate the standard heat of combustion for alkanes, alkenes, alkynes, cyclanes, cyclenes (including terpenes), aromatic hydrocarbons, and polycyclic aromatic hydrocarbons in the liquid state:

$$(\Delta H^\circ_{298})_{comb} = -(104.2n_C + 26.05n_H + 13.0n_= + 46.1n_\equiv +$$

$$+ 6.5n_{=C} - 3.5n_{Ar-Alk} - 6.5n_{Ar-Ar})\ kcal/mol \qquad (1.29)$$

where n_C = number of carbon atoms in a molecule

n_H = number of hydrogen atoms in a molecule

$n_=$ = number of double bonds in a molecule of alkenes or in side chains of cyclic compounds

$n_\equiv$ = number of triple bonds in molecules of alkynes

$n_{=C}$ = number of double bonds in a ring of cyclenes

n_{Ar-Alk} = number of bonds between aryl and alkyl groups

n_{Ar-Ar} = number of bonds between aryl groups.

In calculations for polycyclic aromatic hydrocarbons, n_{Ar-Ar} equals $2(n_{arom.r} - 1)$, where $n_{arom.r}$ is the number of aromatic rings in the polycyclic group. For example for naphthalene $n_{Ar-Ar} = 2$, for phenanthrene it is 4, for chrysene it is 6, etc.

Equation (1.29) gives satisfactory results, but can be recommended, like Eq. (1.28), only for approximate calculations of $(\Delta H^\circ_{298})_{comb}$.

Example 18. Use Eq. (1.28) to calculate the heat of combustion of liquid chlorobenzene at 25 °C and compare it with the experimental value [18] of $(\Delta H^\circ_{298})_{comb} = -743.38$ kcal/mol.

Solution. For C_6H_5Cl, the heat correction $\Delta_i = -6.5$ (Appendix 3), $p = 1$. According to the Kharasch equation

$$(\Delta H^\circ_{298})_{comb} = -26.05 \, (4 \times 6 + 5 - 1) + 1 \, (-6.5) =$$
$$= -735.9 \text{ kcal/mol}$$

which forms a relative error in calculations of 1.01%.

Example 19. Find $(\Delta H^\circ_{298})^{lq}_{comb}$ for ethyl acetate $CH_3COOC_2H_5$ using Kharasch's method.

Solution. According to Appendix 3, the heat correction for the bond in aliphatic esters is -16.5 kcal; the value of p is 4 (two electrons to each atom of oxygen). Hence,

$$(\Delta H^\circ_{298})_{comb} = -26.05 \, (4 \times 4 + 8 - 4) + 1 \, (-16.5) =$$
$$= -537.7 \text{ kcal/mol}$$

The experimental value is -534.98 kcal/mol [18].

Example 20. Calculate $(\Delta H^\circ_{298})^{lq}_{comb}$ for allyl alcohol $CH_2=CHCH_2OH$ by Kharasch's method.

Solution. Two electrons in a molecule of the alcohol are linked to an oxygen atom, therefore $p = 2$. The heat corrections are (a) for the double bond $\Delta_i = -13$ kcal; and (b) for the bond between the primary aliphatic radical and the hydroxyl group (primary alcohol) $\Delta_i = -13$ kcal (Appendix 3). Hence, by Eq. (1.28), we have

$$(\Delta H^\circ_{298})_{comb} = -26.05 \, (4 \times 3 + 6 - 2) - 1 \times 13 -$$
$$- 1 \times 13 = -442.8 \text{ kcal/mol}$$

According to published data [1], $(\Delta H^\circ_{298})_{comb} = -442.6$ kcal/mol.

Example 21. Using Kharasch's method, find $(\Delta H^\circ_{298})^{lq}_{comb}$ for o-nitrotoluene $CH_3C_6H_4NO_2$. Compare the result obtained with the published value of -899.2 kcal/mol [7].

Solution. One electron of a carbon atom is linked to a nitrogen atom and remains there after combustion, therefore $p = 1$. The heat corrections are (a) for the bond of the aromatic and aliphatic radicals $\Delta_i = +3.5$ kcal/mol; and (b) for the bond between the aromatic radical and the NO_2 group $\Delta_i = -13$ kcal/mol. Hence,

$$(\Delta H^\circ_{298})_{comb} = -26.05 \, (4 \times 7 + 7 - 1) - 1 \times 13 + 1 \times$$
$$\times 3.5 = -895.2 \text{ kcal/mol}$$

Example 22. Using Frost's method, calculate $(\Delta H^\circ_{298})^{lq}_{comb}$ for β-methylnaphthalene.

Solution. We have $n_C = 11$, $n_H = 10$, the number of bonds $n_{Ar-Alk} = 1$, the number of bonds $n_{Ar-Ar} = (2 - 1) \times 2 = 2$.

By Eq. (1.29),

$$(\Delta H^{\circ}_{298})_{comb} = -(104.2 \times 11 + 26.05 \times 10 - 3.5 \times 1 -$$
$$- 6.5 \times 2) = -1380.2 \text{ kcal/mol}$$

The experimental value obtained in [38] is $-1383.91 \pm \pm 0.52$ kcal/mol.

1.3.3. Calculation of $(\Delta H^{\circ}_{298})_{comb}$ by the Method of Increments.
Investigation of the available experimental data has shown that
the values of $(\Delta H^{\circ}_{298})_{comb}$ of organic substances belonging to a given
homologous series obey simple laws, for instance the constancy of
the differences between the heats of combustion for the consecutive
members of a homologous series (the increment for the CH_2 group).
Such a constancy of the increments was noted a long time ago by
many authors for various series of substances having an identical
structure. It is quite obvious that quantities relating to the same
state of aggregation have to be compared; a stricter constancy of
the homologous difference should be expected for quantities relating
to the gaseous state when the action of the intermolecular forces can
be considered to be excluded. In many cases, however, the constancy
of the increments is also sufficiently completely observed for data
relating to the liquid, and sometimes to the solid state of substances.
Usually a stricter constancy of the homologous increment is observed
beginning from the fourth or fifth member of a given homologous
series; quite appreciable discrepancies are observed for the first
members of a series.

Thus, $(\Delta H^{\circ}_{298})_{comb}$ for substances belonging to a homologous series
and having a similar structure can be calculated using formulas of
the kind

$$(\Delta H^{\circ}_{298})_{comb} = -(A + Bn) \tag{1.30}$$

where A and B = constants

n = number of carbon atoms.

Equation (1.30) is used when $n > 5$. For example $(\Delta H^{\circ}_{298})_{comb}$
for alkanes of a normal structure can be calculated according to
equations given by M. Karapetyants [12]:

for the gaseous state

$$(\Delta H^{\circ}_{298})_{comb} = -(57.93 + 157.44n) \text{ kcal/mol} \tag{1.31}$$

for the liquid state

$$(\Delta H^{\circ}_{298})_{comb} = -(57.45 + 156.26n) \text{ kcal/mol} \tag{1.32}$$

for the solid state

$$(\Delta H^{\circ}_{298})_{comb} = -(21.90 + 157.00n) \text{ kcal/mol} \tag{1.33}$$

D. Rossini proposes the following equation for the standard heat of combustion of gaseous 1-alkenes at $n > 5$ [3, 39]:

$$(\Delta H^\circ_{298})_{comb} = -(21.90 + 157.00n) \text{ kcal/mol} \qquad (1.34)$$

For many homologous series of organic compounds, the values of the increment for the CH_2 group were found to be the same as have been established for alkanes. Thus, the homologous difference in the heats of combustion of fatty monocarboxylic acids having a normal structure in the liquid state equals 156.3 kcal/mol. J. Green showed [11] that for primary alcohols of a normal structure, beginning from butanol, the constancy of the increment for the CH_2 group is observed with a very high accuracy. This increment equals 157.46 ± 0.02 kcal/mol, i.e. has the same value as for normal alkanes. Owing to the absence of experimental data, the constancy of the increment for the CH_2 group has not been established with such an accuracy for other series of compounds containing functional groups, but we can assume that it will be observed when the CH_2 is sufficiently removed from the functional group.

The constancy of the increment permits us to calculate $(\Delta H^\circ_{298})_{comb}$ for compounds for which there are no experimental data if such data are available for other representatives of the same homologous series. Exact constancy of the homologous difference can be expected, however, only for substances having a similar structure, for instance a normal structure or with branches in the same positions. This greatly limits the use of the law of constant increments.

Example 23. Using the method of increments, assess the standard molar heat of fusion of solid n-decane n-$C_{10}H_{22}$ at 25 °C.

Solution. The melting of n-decane can be represented in the form of the equation

$$n\text{-}C_{10}H_{22}(c) = n\text{-}C_{10}H_{22}(lq), \quad \Delta H_f = ?$$

The molar heat of fusion $(\Delta H^\circ_{298})_f$, according to corollary (1.22) of Hess's law, equals the difference between the standard heats of combustion of the reactants and the products:

$$(\Delta H^\circ_{298})_f = (\Delta H^\circ_{298})^c_{comb} - (\Delta H^\circ_{298})^{lq}_{comb}$$

We use Eqs. (1.33) and (1.32) to find the standard heats of combustion of n-decane at 25 °C in the solid and liquid states:

$$(\Delta H^\circ_{298})^c_{comb} = -(21.90 + 157.00 \times 10) = -1591.9 \text{ kcal/mol}$$

$$(\Delta H^\circ_{298})^{lq}_{comb} = -(57.45 + 156.26 \times 10) = -1620.05 \text{ kcal/mol}$$

We shall note that the experimental value of $(\Delta H^\circ_{298})^{lq}_{comb}$ is -1619.18 kcal/mol [3]. Hence,

$$(\Delta H^\circ_{298})_f = -1591.9 - (-1620.05) = 28.15 \text{ kcal/mol}$$

1.3.4. Tatevsky's Method of Calculating $(\Delta H^{\circ}_{298})_{comb}$. Many methods are known at present that can be used for the accurate calculation of various physicochemical properties of organic substances. They are based on the general principle that the value of a given property is considered to be the sum of the contributions made by separate fragments of a molecule. Such fragments may include separate atoms or groups, separate bonds or a combination of them, or a combination of both kinds of fragments. The contribution of each atom or bond is considered depending on its situation (environment) in the molecule. With such an approach, the value of a given physicochemical property Y is calculated by summation of the products of the number of fragments chosen n_i and the contribution Y_i made by each of them:

$$Y = \sum n_i Y_i \tag{1.35}$$

The number of fragments of a given kind is found on the basis of the structural formula of a molecule, and the contribution of each of them is calculated from experimental data available for separate substances of a given series.

V. Tatevsky [6, 40] proposed a method of calculating the standard heats of combustion and formation from simple substances in the liquid and gaseous state at 25 °C for alkanes of a normal and iso-structure. He distinguished four kinds of C—H bonds in alkane molecules: a zero bond (only in methane), primary, secondary, and tertiary ones, and ten kinds of C—C bonds depending on which carbon atom (primary, secondary, tertiary, or quaternary) is linked with another atom (which may also be primary, secondary, tertiary, or quaternary). Denoting the primary, secondary, tertiary, and quaternary carbon atoms by C_1, C_2, C_3, and C_4, respectively, we obtain the following kinds of C—C bonds in alkanes: C_1—C_1 (only in ethane), C_1—C_2, C_1—C_3, C_1—C_4, C_2—C_2, C_2—C_3, C_2—C_4, C_3—C_3, C_3—C_4, and C_4—C_4. The contributions of the C—H bonds are included in the corresponding C—C bonds, and they do not have to be taken into account separately in the calculations.

Thus, using Tatevsky's scheme for calculating the standard heats of combustion and formation at 25 °C for alkanes, we must have the values of nine constants. Tatevsky found them from available experimental data with the use of the method of least squares (Appendix 4). Letting A with the relevant subscript ($A_{1,2}$, $A_{1,3}$, $A_{1,4}$, $A_{2,2}$, etc.) stand for the contribution of each of the bonds to the total value of the given property, we get the following equation for calculating the standard heat of combustion of alkanes:

$$(\Delta H^{\circ}_{298})_{comb} = \sum n_i A_{i,j} \tag{1.36}$$

where n_i is the number of bonds of a given kind $A_{i,j}$.

Tatevsky's scheme gives results that are very close to experimental data. The only exceptions are alkanes having substituents in the position 2, 2, 4 or 2, 2, 4, 4 (in the latter case the deviations reach 5 kcal/mol). These deviations are explained by steric difficulties caused by the great approach of the methyl groups.

Example 24. Using Tatevsky's scheme, calculate $(\Delta H^\circ_{298})_{comb}$ for liquid 2,3,3-trimethylpentane.

Solution. We depict the skeleton of the compound being considered whose structural formula is

$$
\begin{array}{ccccccc}
& \text{H} & & \text{H} & & & \\
& | & & | & & & \\
\text{H} & \text{H}-\text{C}-\text{H} & \text{H}-\text{C}-\text{H} & & \text{H} & \text{H} & \\
| & | & | & & | & | & \\
\text{H}-\text{C}\!\!-\!\!\!-\!\!\!-\!\!\text{C}\!\!-\!\!\!-\!\!\!-\!\!\text{C}\!\!-\!\!\!-\!\!\!-\!\!\text{C}-\text{C}-\text{H} & & & & & & \\
| & | & | & & | & | & \\
\text{H} & \text{H} & \text{H}-\text{C}-\text{H} & & \text{H} & \text{H} & \\
& & | & & & & \\
& & \text{H} & & & & \\
\end{array}
$$
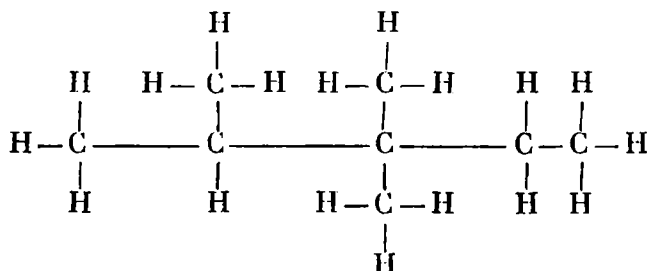
using the subscripts 1, 2, 3, and 4 to denote the primary, secondary, tertiary, and quaternary carbon atoms, respectively:

$$
\begin{array}{cc}
\text{C}_1 & \text{C}_1 \\
| & | \\
\text{C}_1 - \text{C}_3 - \text{C}_4 - \text{C}_2 - \text{C}_1 \\
| \\
\text{C}_1
\end{array}
$$
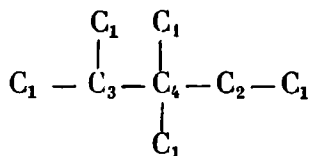
A molecule of this hydrocarbon has the following bonds: C_1-C_2 — one, C_1-C_4—two, C_2-C_4—one, C_1-C_3—two, and C_3-C_4—one. According to Eq. (1.36), the standard heat of combustion of 2,3,3-trimethylpentane is (Appendix 4)

$$-(\Delta H^\circ_{298})^{lq}_{comb} = A_{1,2} + 2A_{1,3} + 2A_{1,4} + A_{2,4} + A_{3,4} =$$
$$= 263.24 + 2 \times 226.99 + 2 \times 208.68 + 102.70 + 68.90 =$$
$$= 1306.18 \text{ kcal/mol}$$

Hence, $(\Delta H^\circ_{298})^{lq}_{comb} = -1306.18$ kcal/mol.

The experimental value [6] is -1306.64 ± 0.31 kcal/mol. The difference is 0.46 kcal/mol which is very close to the error of experimental data.

1.3.5. Laidler's Method of Calculating $(\Delta H^\circ_{298})_{comb}$. Tatevsky's scheme considered above shows the possibility of calculating the

standard heats of combustion and formation of alkanes from simple substances with a high accuracy. Alkanes have only two kinds of bonds: ordinary C—C bonds and C—H bonds. True, all the C—C and C—H bonds cannot be considered equivalent with respect to energy.

Matters become considerably more complicated when passing over to the other classes of organic compounds, and the number of constants needed for calculating ΔH sharply grows. For example when using Tatevsky's method for alkenes, 21 constants are already needed (instead of 9 for alkanes). These constants can be calculated only when a large amount of reliable experimental data are available. Such data, apart from alkenes, are available at present only for a very small number of series of organic compounds. In most cases, the calculations have to be conducted using rougher approximations. The following procedure is often employed: the contributions of the hydrocarbon portion of a molecule are assessed separately while the corresponding increment found from available experimental data is added to the contributions of the functional groups. We shall consider the method proposed by K. Laidler [41, 42] as an example of such calculations. Laidler considers that all the C—C bonds in alkanes are equivalent, and classifies the C—H bonds as primary (the hydrogen is linked to a primary carbon atom), secondary (to a secondary atom), and tertiary (to a tertiary carbon atom). Thus, only four parameters are needed to calculate the properties of any alkane.

In calculating ΔH for alkenes and alkynes, we must take into consideration the remoteness of the double and triple bonds from the C—H bonds.

Appendix 5 gives the contributions of separate bonds and atomic groups to the values of the standard heats of combustion and formation at 25 °C. This Appendix uses the following classification of the C—H bonds: p, s, and t are primary, secondary, and tertiary bonds removed from a double (or triple) one by more than one bond; p', s', and t' are bonds removed from a double (or triple) one by one bond; and p_2, s_2, and t_3 are bonds adjoining a double or triple one. The figures given in parentheses in Appendix 5 have been calculated on the assumption that the contribution of a given bond to the heat is not affected by the presence of double or triple bonds in a molecule.

We must again stress the fact that the values calculated with the aid of Appendix 5 cannot claim a high accuracy: first, because Laidler's scheme itself is a quite rough approximation, and, second, because many increments are taken from insufficiently reliable experimental data.

Example 25. Using Laidler's method, calculate $(\Delta H^\circ_{298})_{comb}$ for liquid 2,3-dimethylpentane.

Solution. A molecule of 2,3-dimethylpentane has the following structure:

$$CH_3 - CH - CH - CH_2 - CH_3$$
$$| |$$
$$CH_3 CH_3$$
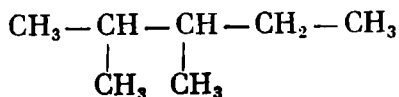
The molecule contains six C—C bonds, 12 primary C—H bonds, two secondary C—H bonds, and two tertiary C—H bonds. Hence,

$$(\Delta H^\circ_{298})_{comb} = 6c + 12p + 2s + 2t$$

Using Appendix 5, we get

$$(\Delta H^\circ_{298})^{lq}_{comb} = 6\,(-47.48) + 12\,(-53.73) + 2\,(-54.46) +$$
$$+ 2\,(-55.37) = -1129.30 \text{ kcal/mol}$$

The experimental value [6] is -1149.09 ± 0.28 kcal/mol, and that calculated by Tatevsky's method is -1150.22 kcal/mol. The value of $(\Delta H^\circ_{298})^{lq}_{comb}$ found by Laidler's method differs considerably from the experimental value.

B. Methods of Calculating the Standard Heats of Formation of Organic Compounds from Simple Substances $(\Delta H^\circ_{298})_{form}$ at 25 °C

1.3.6. Calculation of $(\Delta H^\circ_{298})_{form}$ of Organic Substances in the Gaseous State from the Bond Energies. Many authors attempted to construct a scheme for calculating $(\Delta H^\circ_{298})_{form}$ on the basis of the prevailing ideas on the energy of the separate chemical bonds in a molecule.

This method is based on the assumption that the energy of formation of one mole of a given substance in the gaseous state from isolated atoms equals the sum of the energies of all the chemical bonds formed in a molecule of the substance. The general form of the equation is as follows:

$$A_a B_b C_c = aA \text{ (g)} + bB \text{ (g)} + cC \text{ (g)} + \ldots, \quad \Delta H_{at} \qquad (1.37)$$

where $A_a B_b C_c$ = molecule of the corresponding composition
     A, B, C = isolated atoms
     a, b, c = stoichiometric coefficients
     ΔH_{at} = atomic heat of formation.

It is easy to find the value of ΔH_{at} for many substances on the basis of thermochemical data. This quantity, however, gives nothing except the sum of the energies of all the chemical bonds in a molecule and does not permit us to reach a conclusion on the energy of each bond separately.

The bond energies are used for calculations by introducing the wittingly approximate assumption that the values of these energies remain unchanged when passing over from one molecule to another. In this case, the possibility is provided of consecutively determining the energy of separate bonds by finding them from ΔH_{at} for the very simple molecules and using them to calculate others. For example, knowing ΔH_{at} for two saturated hydrocarbons, we can find the energy of the C—C and C—H bonds separately. Using these values, we can, for instance, find the energy of the C—Cl bond if we know ΔH_{at} for at least one of the chloroderivatives of the alkanes. By consecutively following this path, we can determine the energy of all the remaining chemical bonds.

This simple procedure may lead to improper results, however. It must be indicated first of all that the very concept of the energy of a bond has a clear physical meaning only for a diatomic molecule with one chemical bond. In this case, the bond energy equals the energy of dissociation of the given molecule into atoms. For molecules having several bonds of the same kind (H_2O, NH_3, CH_4, and the like), all the bonds should be considered equivalent and the corresponding fraction of ΔH_{at} taken as the value of the energy of the separate bonds. For example, one-fourth of ΔH_{at} for methane is taken as the bond energy for CH_4. The values of the bond energy found in this way are certain mean values and do not correspond to the quantity of energy that must be spent to break a given atom away from a molecule. The concept of the energy of separate bonds in molecules containing different kinds of bonds becomes even more obscure. Therefore, the bond energies found in this way should be considered only as certain effective values that are intended for use in calculations of the standard heats of formation at a temperature of 25 °C.

In view of the above, the calculation of $(\Delta H_{298}^{\circ})_{form}$ according to bond energies leads only to comparatively rough results, but owing to the lack of other general methods of calculating thermochemical quantities, the method of bond energies is widely used at present. On previous pages, we have already considered some methods of calculating $(\Delta H_{298}^{\circ})_{form}$ with the use of bond energies (see Tatevsky's and Laidler's methods). Now we shall deal with the method of calculating $(\Delta H_{298}^{\circ})_{form}$ according to the bond energies with the use of Hess's law.

The synthesis of a compound from simple substances can be identified with the process of their consecutive conversion into monoatomic gases with the following formation of a compound from them. The first stage is connected with the expenditure of energy for breaking the bonds, and the second with the liberation of energy for the formation of the new bonds. Therefore, the heat of formation of a gaseous substance in accordance with Hess's law can be found by

the equation

$$(\Delta H_{298}^{\circ})_{\text{form}} = \sum (\nu_i \varepsilon_i)_r + \sum n_i (Q_{\text{subl}})_i - \sum (\nu_i' \varepsilon_i)_{\text{pr}} \qquad (1.38)$$

where ν_i and ν_i' = number of bonds of a given kind in the reactants
and the products
ε_i = bond energy corresponding to them
n_i = number of different atoms of the solid reactants
$(Q_{\text{subl}})_i$ = heats of sublimation corresponding to them.
The values of the energies of selected bonds found from the heats
of formation and combustion of compounds or from spectral data
are given in Appendix 6. Similar tables given in many textbooks,
reference books, monographs, and guides contain values that fre-
quently differ from one another. One reason is the discrepancy in
the values of the energy of sublimation of carbon (beta-graphite)
serving as the basis of the calculations. To date, this value cannot
be considered as accurately established (different authors give its
value either equal to 125 [8] or 171.3 kcal/g·atom [43]). These dis-
crepancies are of no importance for the practical use of the tables
because the influence of these values is eliminated upon the reverse
calculation of the heats of formation of compounds from simple sub-
stances with the aid of any of these tables. A second more significant
reason for the discrepancies (less considerable) are the different
sets of initial data on which separate tables are based.
The most reliable results of calculations by Eq. (1.38) are obtained
for alkanes and alcohols. Calculations give unsatisfactory results
for cyclic structures.
Appendix 6 contains the mean values of bond energies obtained
by a number of authors. Calculations of $(\Delta H_{298}^{\circ})_{\text{form}}$ according to
the bond energies result in errors ranging from one to five kcal/mol
for various organic compounds. The accuracy of such calculations
grows sharply if we take into account how the energy of a given bond
is affected by its environment in a molecule, namely the kinds of
bond of a carbon atom participating in the bond being studied with
other atoms, and the nature of the atoms linked to the carbon atom.
We considered this influence in detail when describing Tatevsky's
and Laidler's methods.
Equation (1.38) also permits us to calculate the standard heat
of any chemical reaction at a temperature of 25 °C (ΔH_{298}°) in addi-
tion to the standard heat of formation from simple substances.

Example 26. Calculate $(\Delta H_{298}^{\circ})_{\text{form}}$ for *n*-butane according to the
bond energies.
Solution. The formation of *n*-butane from simple substances follows
the equation

$$4\text{C (graphite)} + 5\text{H}_2(\text{g}) = n\text{-C}_4\text{H}_{10}(\text{g})$$

Hence,

$$(\Delta H^\circ_{298})^g_{form} = 5\varepsilon_{H-H} + 4Q_{subl,\,C} - (3\varepsilon_{C-C} + 10\varepsilon_{C-H})$$

We find the values of the corresponding bond energies and the heat of sublimation of graphite in Appendix 6. The required value is

$$(\Delta H^\circ_{298})_{form} = 5 \times 103.2 + 4 \times 125 - (3 \times 62.8 + 10 \times$$
$$\times 85.6) = -28.4 \text{ kcal/mol}$$

The value of $(\Delta H^\circ_{298})_{form}$ for *n*-butane given in a reference book [20] is -30.15 kcal/mol. Consequently, the relative error of the calculations is 5.81%.

Example 27. Find $(\Delta H^\circ_{298})_{form}$ for CH_3COOH in the gaseous state. Use Appendix 6 for the calculations.

Solution. The formation of CH_3COOH follows the equation

$$2H_2(g) + O_2(g) + 2C(c) = CH_3COOH(g)$$
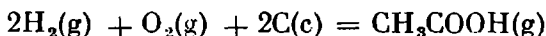
The formation of CH_3COOH from simple substances is attended by the breaking of two H—H bonds, one O—O bond, the sublimation of two gramme-atoms of C, and the formation of three C—H bonds, one C—C bond, and one —COOH group. Hence,

$$(\Delta H^\circ_{298})_{form} = 2\varepsilon_{H-H} + \varepsilon_{O-O} + 2Q_{subl,\,C} - 3\varepsilon_{C-H} - \varepsilon_{C-C} - \varepsilon_{-COOH}$$

Introducing the values of the bond energies found in Appendix 6, we get

$$(\Delta H^\circ_{298})^g_{form} = 2 \times 103.2 + 117.2 + 2 \times 125 -$$
$$- 3 \times 85.6 - 62.8 - 360 = -106.0 \text{ kcal/mol}$$

According to published data [20] this value is -104.3 kcal/mol.

Example 28. Determine $(\Delta H^\circ_{298})_{form}$ for gaseous methyl iodide using the method of bond energies.

Solution. The reaction of formation of CH_3I is
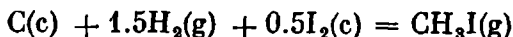
$$C(c) + 1.5H_2(g) + 0.5I_2(c) = CH_3I(g)$$
$$(\Delta H^\circ_{298})^g_{form} = Q_{subl,\,C} + 1.5\varepsilon_{H-H} + 0.5Q_{subl,\,I_2} + 0.5\varepsilon_{I-I} -$$
$$- 3\varepsilon_{C-H} - \varepsilon_{C-I}$$
$$(\Delta H^\circ_{298})_{form} = 125 + 1.5 \times 103.2 + 0.5 \times 14.88 + 0.5 \times$$
$$\times 35.6 - 3 \times 85.6 - 43 = +5.2 \text{ kcal/mol}$$

According to published data, $(\Delta H^\circ_{298})_{form} = 4.9$ kcal/mol [20].

Example 29. Use the bond energies to find the standard heat of the reaction

$$C_3H_6(g) + H_2O(g) = iso\text{-}C_3H_7OH(g)$$
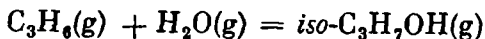
proceeding in the gaseous phase at 298.15 K.

Compare the result of the calculations with the value of ΔH°_{298} computed according to the corollary of Hess's law [Eq. (1.22)] if the values of $(\Delta H^\circ_{298})_{form}$ for the reagents are 4.879, —57.798, and —64.2 kcal/mol, respectively (Appendix 1).

Solution. According to Eq. (1.38) and Appendix 6, we have

$$\Delta H^\circ_{298} = (\varepsilon_{C-C} + \varepsilon_{C=C} + 6\varepsilon_{C-H} + 2\varepsilon_{O-H}) -$$

$$- (2\varepsilon_{C-C} + 7\varepsilon_{C-H} + \varepsilon_{C-O} + \varepsilon_{O-H})$$

$$\Delta H^\circ_{298} = (62.8 + 101.2 + 6 \times 85.6 + 2 \times 110) -$$

$$- (2 \times 62.8 + 7 \times 85.6 + 75 + 110) = -12.2 \ \text{kcal}$$

The same quantity can be calculated by Eq. (1.22):

$$\Delta H^\circ_{298} = -64.2 - (4.879 - 57.798) = -11.28 \ \text{kcal}$$

The result of the calculations according to the bond energies differs from the value of ΔH°_{298} determined from the heats of formation by 0.92 kcal/mol (8.13%).

1.3.7. Calculation of $(\Delta H^\circ_{298})_{form}$ of Hydrocarbons by the Method of Increments. We have already noted that for the successive members of a homologous series for a number of hydrocarbons the differences between the values of the heats of combustion or formation, the so-called increment per $-CH_2$ group, are constant. The standard heats of formation of substances of a homologous series having a similar structure are calculated by formulas of the kind

$$(\Delta H^\circ_{298})_{form} = -(A + Bn) \tag{1.39}$$

where A and B = constants

n = number of carbon atoms in a molecule.

Equation (1.39) can usually be applied when n exceeds five.

Work conducted by F. Rossini and his co-workers [1] resulted in the possibility appearing of calculating the standard heats of formation at 25 °C of gaseous and liquid n-alkanes, gaseous 1-alkenes, n-alkylcyclopentanes, n-alkylcyclohexanes, and n-alkylbenzenes with a high accuracy. Below are given equations compiled on the basis of best available calorimetric investigations with the aid of the method of least squares. These equations include a quantity with an accuracy to which $(\Delta H^\circ_{298})_{form}$ is calculated.

For gaseous n-alkanes $(n > 5)$

$$(\Delta H^\circ_{298})^g_{form} = -10\ 408 - 4926n \ \pm$$

$$\pm\ (164.8 - 38.64n \pm 2.893n^2)^{1/2} \ \text{cal/mol} \tag{1.40}$$

For liquid n-alkanes $(n > 5)$

$$(\Delta H^{\circ}_{298})^{lq}_{form} = -10\,887 - 6106n \pm$$

$$\pm\,(165.4 - 38.98n \pm 2.903n^2)^{1/2} \text{ cal/mol} \tag{1.41}$$

For gaseous 1-alkenes having a normal structure $(n > 5)$

$$(\Delta H^{\circ}_{298})^{g}_{form} = 19\,592 - 4926n \pm$$

$$\pm\,(324.8 - 38.84n \pm 2.893n^2)^{1/2} \text{ cal/mol} \tag{1.42}$$

For gaseous n-alkylcyclopentanes $(n > 8)$

$$(\Delta H^{\circ}_{298})^{g}_{form} = 4114 - 4926n \pm$$

$$\pm\,(360.5 - 58.64n \pm 3.637n^2)^{1/2} \text{ cal/mol} \tag{1.43}$$

For gaseous n-alkylcyclohexanes $(n > 9)$

$$(\Delta H^{\circ}_{298})^{g}_{form} = -1690 - 4926n \pm$$

$$\pm\,(421.6 - 63.58n \pm 3.637n^2)^{1/2} \text{ cal/mol} \tag{1.44}$$

For gaseous n-monoalkylbenzenes $(n > 9)$

$$(\Delta H^{\circ}_{298})^{g}_{form} = 45\,960 - 4926n \pm$$

$$\pm\,(423.4 - 66.11n \pm 3.637n^2)^{1/2} \text{ cal/mol} \tag{1.45}$$

Example 30. Use the method of increments to calculate the value of $(\Delta H^{\circ}_{298})_{form}$ of gaseous 1-decene $(C_{10}H_{20})$. Compare the value obtained with the published one [20] equal to $-29\,670$ cal/mol. *Solution.* We use Eq. (1.42). For 1-decene $n = 10$. Hence,

$$(\Delta H^{\circ}_{298})^{g}_{form} = 19\,592 - 4926 \times 10 \pm$$

$$\pm\,(324.8 - 38.84 \times 10 \pm 2.893 \times 10^2)^{1/2} =$$

$$= -29\,678 \pm 15 \text{ cal/mol}$$

The calculated value differs from the published one by $8 \pm$ $\pm\,15$ cal/mol.

1.3.8. Calculation of $(\Delta H^{\circ}_{298})_{form}$ of Gaseous Organic Compounds by the Method of Introducing Corrections for the Substitution of Hydrogen by $-CH_3$ and Other Groups. The empirical method proposed by J. Anderson, G. Beyer, and K. Watson [44-46] makes it possible to calculate with sufficient accuracy the standard heat of formation at 25 °C, the absolute value of the entropy in the standard state at 25 °C (S°_{298}), and the temperature dependence of the heat capacity $C^{\circ}_p = a + bT + cT^2$ for virtually any organic compounds (heterocyclic compounds are an exception). Checking of this method

showed that the results of calculating $(\Delta H^{\circ}_{298})_{form}$ differ from the best experimental data by not more than 4.0 kcal/mol. In the calculations, each compound is assumed to consist of a basic group which is modified by the substitution of the atoms forming it by other groups.

Appendix 7 gives all the data needed for the calculations. Appendix 7a gives the properties of the basic groups of ten hydrocarbons. Appendix 7b gives corrections (contributions) for the primary substitution of hydrogen of the basic group by $-CH_3$. The corrections depend on the number of substitutions and the position of the atom being substituted. Appendix 7c gives corrections for secondary substitutions of hydrogen by a $-CH_3$ group. To determine the corresponding corrections, it is necessary to know the so-called type numbers of the carbon atom at which the substitution takes place (a type A atom) and the less hydrogenated carbon atom adjacent to it (a type B atom). The type numbers of the carbon atoms are determined according to the number of hydrogen atoms linked to a carbon atom as shown below:

Radical	$-CH_3$	$= CH_2$	$-\overset{\mid}{C}H-$	$-\overset{\mid}{\underset{\mid}{C}}-$	$= C -$
Type	1	2	3	4	5
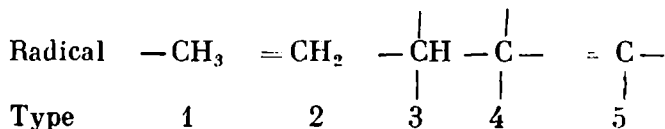
Type 5 relates to a carbon atom of a benzene or naphthalene ring.

The same Appendix 7c gives corrections for calculating the properties of ethers and esters. One of the corrections is given for the substitution of the hydrogen of a hydroxyl group by a $-CH_3$ group with the formation of methyl ether or ester, and the other for the substitution of the carboxyl hydrogen in carboxylic acid by a $-CH_3$ group with the formation of ethyl ester. Appendix 7d gives corrections for the substitution of single bonds by double and triple ones. The data of Appendix 7e take into account the length of a side chain in cyclic hydrocarbons and the position of the double bond. Finally, Appendix 7f gives corrections for the substitution of the $-CH_3$ group by any other group. The table includes the phenyl group $-C_6H_5$ which can be considered as the basic one in calculating the properties of complex compounds where several groups are combined, for instance in polybasic aromatic acids.

Corrections to the heats of formation taking into account the primary substitution of a $-CH_3$ group by chlorine have not been found to date. It has been noted, however, that the heat of formation changes with each following substitution by chlorine at the initial carbon atom.

Attention must be given to the necessity of adding an additional correction ($+1.0$ cal/K·mol) to the calculated corrections when determining the entropy of halogen derivatives of alkanes.

The sequence of calculating the thermodynamic properties of complex organic compounds according to the method being considered is as follows.

1. Appendix 7a is used to choose the substance which is the basis of the compound being considered. If there is a choice of the basic substances, the one having the highest value of the entropy should be selected.

2. For cyclic hydrocarbons having more than six carbon atoms in the ring, cyclohexane is selected as the basic group, and the ring is expanded with account taken of the data of Appendix 7b (item 3a).

3. All the primary substitutions must be completed before beginning the secondary ones. Here Appendix 7b must be used. Only one primary substitution is possible for methane. For a cyclic structure, one primary substitution may be performed for each carbon atom in the ring. If more than two primary substitutions are to be made in the main ring, the two closest substitutions are made first. If more than one substitution is to be made at a carbon atom in the main ring, the following substitutions are conducted as secondary ones, and they are made only after all the primary substitutions have been dealt with.

4. A complete skeleton of the compound is constructed, conducting consecutive secondary substitutions of a hydrogen atom by a $-CH_3$ group with the aid of Appendix 7b. Here the following rules should be observed:

(a) first the longest straight chain is constructed;

(b) the side chains are introduced in the order of their length; however, if the carbon atom having the longest side chain is to have a second side chain, this chain is introduced before the substitutions are made at the other carbon atoms of the main group; if the same compound can be obtained by different substitutions, for example by introducing the side $-CH_3$ groups clockwise or counterclockwise, the average result is taken;

(c) if a chain has several double bonds, the one closest to the end of the chain is introduced first.

5. The $-CH_3$ groups are introduced which will later be substituted by the relevant groups according to Appendix 7f. When introducing these $-CH_3$ groups, the corrections are taken in accordance with Appendix 7c.

6. The single bonds are substituted by double or triple ones in accordance with Appendix 7d.

7. If necessary, the additional corrections provided for by Appendix 7e are introduced.

8. Substitutions are conducted according to Appendix 7f.

9. After summation of all the corrections (called contributions by some authors), the value of the required thermodynamic property of the organic compound is obtained.

Example 31. Using the method of introducing corrections for the substitution of hydrogen by $-CH_3$ and other groups, find $(\Delta H^{\circ}_{298})_{form}$ for gaseous 2,2,4-trimethylpentane. Compare the result of the calculations with the value given in a reference book.

Solution. We shall take methane, for which $(\Delta H^{\circ}_{298})_{form} = -17.89$ kcal/mol (Appendix 7a), as the basic substance. In accordance with the recommendations on how to apply the method, we consecutively construct the longest chain consisting of five carbon atoms. For this purpose, we first introduce a correction for the primary substitution of hydrogen by the $-CH_3$ group (Appendix 7b), and then make three secondary substitutions of hydrogen by the $-CH_3$ group (Appendix 7c). The corrections for the secondary substitutions are introduced with account taken of the type numbers of the carbon atoms.

A scheme showing how the longest carbon chain is constructed is given below:

$$\underset{\Delta H \,=\, -\,17.89}{CH_4} \quad \xrightarrow[\Delta(\Delta H)=-2.50]{} \quad \overset{(B) \quad (A)}{CH_3 - CH_3} \quad \xrightarrow[\Delta(\Delta H)=-4.75]{(A)=1, (B)=1} \quad$$

$$\rightarrow \overset{(B) \qquad (A)}{CH_3 - CH_2 - CH_3} \quad \xrightarrow[\Delta(\Delta H)=-4.92]{(A)=1, (B)=2} \quad$$

$$\rightarrow \overset{(B) \qquad\qquad (A)}{CH_3 - CH_2 - CH_2 - CH_3} \quad \xrightarrow[\Delta(\Delta H)=-4.92]{(A)=1, (B)=2} \quad$$

$$\rightarrow CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$
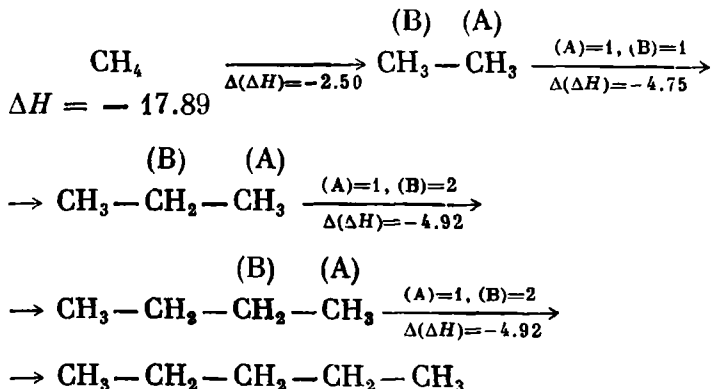
After constructing the longest carbon chain of the molecule being considered (which we have already done), we begin to introduce the side chains in the order of their length. In the given case, all the side chains are identical. Therefore, we can introduce them in any order, performing secondary substitutions of hydrogen by $-CH_3$ groups:

$$\overset{(B) \quad\ (A) \quad\ (B)}{CH_3 - CH_2 - CH_2 - CH_2 - CH_3} \quad \xrightarrow[\Delta(\Delta H)=-6.33]{(A)=2, (B)=2} \quad$$

$$\rightarrow \overset{(B)}{\underset{\underset{(B) \quad\ (A) \quad\ (B)}{}}{CH_3 - \overset{\overset{\textstyle CH_3}{\big|}}{CH} - CH_2 - CH_3}} \quad \xrightarrow[\Delta(\Delta H)=-7.00]{(A)=3, (B)=2} \quad$$

$$CH_3$$
$$\quad | \quad (B) \qquad (A) \qquad (B)$$
$$\rightarrow CH_3 - C - CH_2 - CH_2 - CH_3 \xrightarrow[\Delta(\Delta H)=-6.33]{(A)=2,\ (B)=2}$$
$$\quad | \quad$$
$$CH_3$$

$$CH_3 \qquad\qquad CH_3$$
$$\quad | \qquad\qquad | \quad$$
$$\rightarrow CH_3 - C - CH_2 - CH - CH_3$$
$$\quad | \quad$$
$$CH_3$$
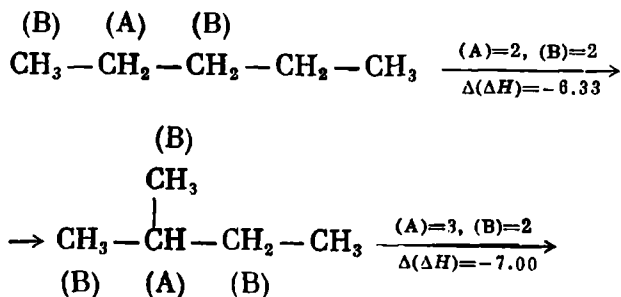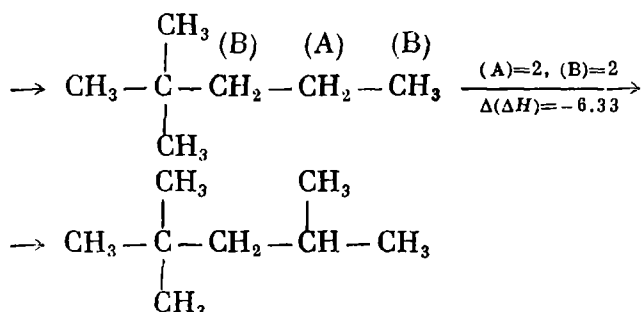
Thus, by consecutively substituting hydrogen by $-CH_3$ groups, we have obtained 2,2,4-trimethylpentane for which the required thermodynamic property is determined by summation of the thermodynamic properties of the basic group and all the corrections:

$$(\Delta H^\circ_{298})^g_{\text{form}} = -17.89 - 2.50 - 4.75 - 4.92 - 4.92 -$$
$$- 6.33 - 7.00 - 6.33 = -54.64 \text{ kcal/mol}$$

According to the data of M. Karapetyants [20], the value of this quantity is -53.57 kcal/mol.

Example 32. Using the method of Anderson, Beyer, and Watson, calculate $(\Delta H^\circ_{298})_{\text{form}}$ for gaseous acetone (dimethylketone). Compare the result obtained with the value of $(\Delta H^\circ_{298})_{\text{form}} = -51.72$ kcal/mol given by F. Rossini et al [2].

Solution. We shall depict the construction of an acetone molecule $\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}\!\!>\!\!C=O$ according to the following scheme:

$$\qquad\qquad\qquad\qquad (A) \quad (B)$$
$$CH_4 \xrightarrow[\Delta(\Delta H)=-2.50]{} CH_3 - CH_3 \xrightarrow[\Delta(\Delta H)=-4.75]{(A)=1,\ (B)=1}$$
$$\Delta H = -17.89$$

$$\quad (B) \quad (A) \quad (B)$$
$$\rightarrow CH_3 - CH_2 - CH_3 \xrightarrow[\Delta(\Delta H)=-6.31]{(A)=2,\ (B)=1}$$

$$\quad (B) \quad (A) \quad (B)$$
$$\rightarrow CH_3 - CH - CH_3 \xrightarrow[\Delta(\Delta H)=-8.22]{(A)=3,\ (B)=1}$$
$$\qquad\qquad |$$
$$\qquad\qquad CH_3$$
$$\qquad (B)$$

$$\qquad CH_3 \qquad\qquad\qquad CH_3$$
$$\qquad | \qquad\qquad\qquad\qquad \backslash$$
$$\rightarrow CH_3 - C - CH_3 \xrightarrow[\Delta(\Delta H)=-13.20]{} \quad C = O$$
$$\qquad | \qquad\qquad\qquad\qquad /$$
$$\qquad CH_3 \qquad\qquad\qquad CH_3$$
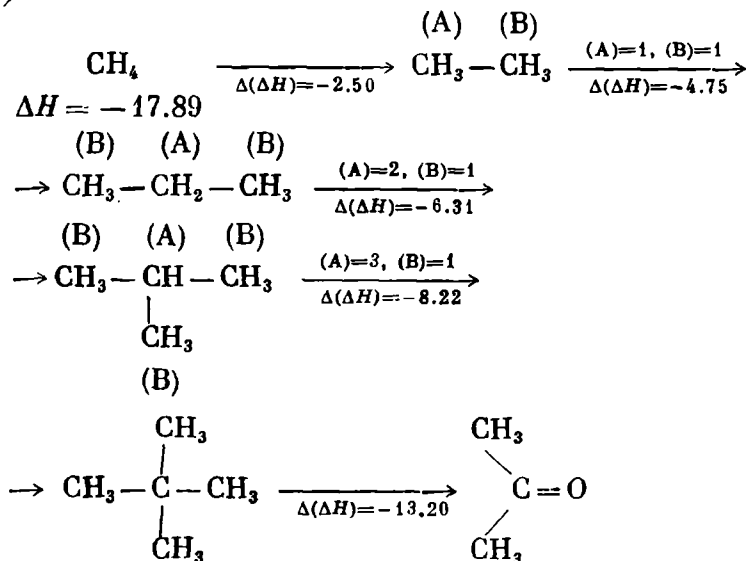
Hence,

$$(\Delta H^\circ_{298})_{form} = -17.89 - 2.50 - 4.75 - 6.31 - 8.22 - 13.20 =$$
$$= -52.87 \text{ kcal/mol}$$

A comparison of the calculated and published values of $(\Delta H^\circ_{298})_{form}$ [2] points to their satisfactory similarity.

Example 33. Assess the value of $(\Delta H^\circ_{298})^f_{form}$ for dimethylphthalate
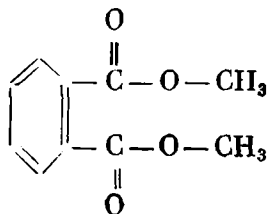
Use Appendix 7 for the calculations.

Solution. We determine the required value of the given thermodynamic property—the heat of formation of dimethylphthalate—by the method of introducing corrections for the substitution of hydrogen by $-CH_3$ and other groups:
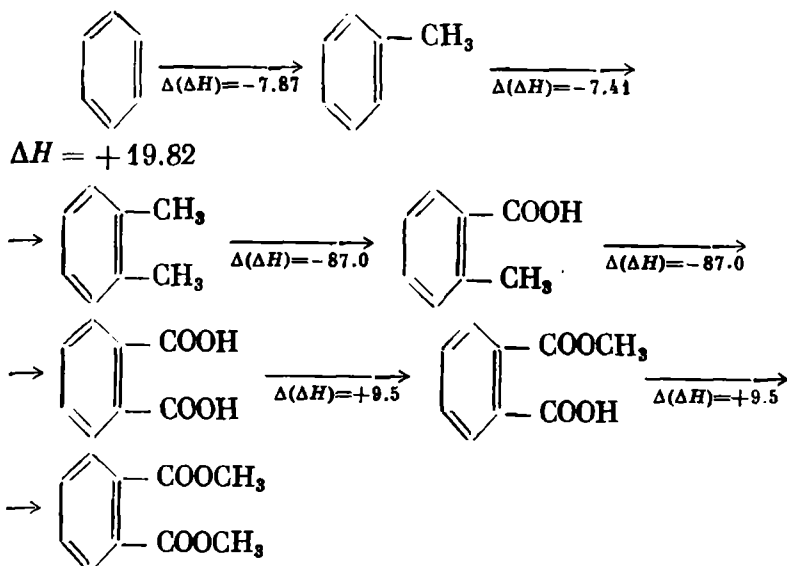
The required value is

$$(\Delta H^\circ_{298})^f_{form} = 19.82 - 7.87 - 7.41 - 87.0 - 87.0 +$$
$$+ 9.5 + 9.5 = -150.46 \text{ kcal/mol}$$

The published value [2] is −147.1 kcal/mol.

1.3.9. Maslovs' Method of Calculating $(\Delta H^{\circ}_{298})_{\text{form}}$. A special place among the approximate methods of calculating the thermodynamic quantities is occupied by methods permitting us to use a small amount of initial data for the simplest compounds of a homologous series to find the thermodynamic properties for all the remaining compounds of a given series. Among the latter is the method proposed by P. and Yu. Maslov [47-50].

It is known that the thermodynamic properties of substances can be calculated from spectral data if the structure of the molecules of these substances and their vibrational spectra are known. A method was proposed for calculating the thermodynamic properties of organic and inorganic compounds without knowing their vibrational spectra. The authors of the method showed that the vibrational spectra have additive properties. This makes it possible to use the known structure and vibrational spectra of several substances to calculate the lacking data for the entire homologous series of compounds using the following equation:

$$Y_i = \frac{1}{n} \sum_j \delta_j Y_j \qquad (1.46)$$

where Y = value of the property of interest to us

i and j = conditional symbol of the chemical formula of the compound $AR_i X^i_{a_i}$ of interest to us and the initial compound $AR_i X^i_b$

$n = \sum_i \delta_j$ = maximum valence of the coordinating group A which is identical for all the members of the series

δ_j = coefficient.

Equation (1.46) for the homologous series of various organic compounds can be written in the form

$$Y_{AR_k R_m \ldots R_q} = \frac{1}{n} \left(kY_{AR'_k} + mY_{AR''_m} + \ldots + qY_{AR'_q} \right). \qquad (1.47)$$

where A stands for the basic group of a homologous series (for example CH_4 or C_6H_6), and R is any functional group introduced into the basic group (for example F, Cl, CH_3 or C_6H_5).

In Eqs. (1.46) and (1.47), n is the maximum valence of the basic group (for example for CH_4 we have $n = 4$, and for C_6H_6 we have $n = 6$).

Equations (1.46) and (1.47) can be used for approximate calculations of $(\Delta H^{\circ}_{298})_{\text{comb}}$ and $(\Delta H^{\circ}_{298})_{\text{form}}$.

Thus, for calculating the approximate value of a thermodynamic property by Eq. (1.47), we must know exactly the values of this property for the initial compounds of the homologous series and one or two other representatives of the series. For instance to cal-

culate $(\Delta H^\circ_{298})_{form}$ for all the halomethanes, we must know with sufficient accuracy the value of this quantity for the five initial members, namely, CH_4, CF_4, CCl_4, CBr_4, and CI_4. It will be still better if we know the values of this quantity for halomethanes of the kind CH_2Hal_2. To calculate the values of $(\Delta H^\circ_{298})_{form}$ for all the haloethylenes, we must know the values of this quantity for C_2H_4, C_2Cl_4, C_2F_4, C_2Br_4, C_2I_4, or for $C_2H_2Hal_2$.

The authors of the method being discussed indicate that its accuracy mainly depends on that of the corresponding thermodynamic properties of the initial compounds.

Maslovs' method can also be used for the solid and liquid phases.

Equation (1.46) can be employed for calculating other thermodynamic properties of gaseous organic compounds. Thus, the standard entropy S°_{298} and the standard Gibbs energy of formation $(\Delta G^\circ_{298})_{form}$ are determined by the equation

$$Y_i = \frac{1}{n} \sum_j \delta_j Y_j - \Delta M - \Delta D + \Delta \sigma \qquad (1.48)$$

where

$$\Delta M = \frac{3R}{2n} \left(\sum_j \delta_j \ln M_j - n \ln M_i \right) \qquad (1.49)$$

Here M is the molecular weight of a substance, and R is the molar gas constant;

$$\Delta D = \frac{R}{2n} \left(\sum_j \delta_j \ln D_j - n \ln D_i \right) \qquad (1.50)$$

where D are the products of the principal moments of inertia of the molecules;

$$\Delta \sigma = \frac{R}{n} \left(\sum_j \delta_j \ln \sigma_j - n \ln \sigma_i \right) \qquad (1.51)$$

where σ are the symmetry numbers of the molecules.

The values of the products of the principal moments of inertia D and the symmetry numbers σ can be found in reference books [51]. For the products of the principal moments of inertia of halomethanes and their symmetry numbers [49] see Appendix 8.

For such thermodynamic properties as the heat capacity, enthalpy, and also $(\Delta H^\circ_{298})_{comb}$ and $(\Delta H^\circ_{298})_{form}$, the addends ΔM, ΔD, and $\Delta \sigma$ are absent in Eq. (1.48), and the required properties are found directly by Eq. (1.46).

Of great practical interest are the equations for the temperature dependence of the heat capacity at constant pressure C°_p of vapours of various homologous series of organic compounds proposed by P. Maslov [47, 48]. These equations, which hold for a quite broad

range of temperatures, have the following general form:

$$C_p^o = a + b \times 10^{-3}T + c \times 10^{-6}T^2 + d \times 10^{-9}T^3 +$$
$$+ C_2(T)\, z + C_3(n, m, T) \text{ cal/mol·K} \tag{1.52}$$

where $a, b, c, d =$ coefficients of the temperature dependence of the heat capacity

$C_2(T) =$ fraction falling to each of the methylene and methyl groups CH_2 of a linear hydrocarbon chain identical for all classes of compounds:

$$C_2(T) = 0.1203 + 21.3 \times 10^{-3}T - 11.633 \times 10^{-6}T^2 +$$
$$+ 2.502 \times 10^{-9}\, T^3 \tag{1.53}$$

$z =$ number of methylene and methyl groups in the linear hydrocarbon chain of a molecule

$C_3(n, m, T) =$ coefficient depending on the number of carbon atoms n, the number of hydrogen atoms m in a molecule, and on the temperature T (it is usually taken into account when calculating the heat capacities of the first five simplest compounds of each homologous series).

P. Maslov [48] gives the following temperature dependences of the true molar heat capacity at constant pressure:

for n-alkanes

$$C_p^o = -1.1583 + 8.272 \times 10^{-3}T - 1.597 \times 10^{-6}T^2 -$$
$$- 0.416 \times 10^{-9}T^3 + C_2(T)\, n + 244.51n^{-1}(2n + 2)^{-2} \times$$
$$\times e^{-0.007T} \tag{1.54}$$

for n-alkenes

$$C_p^o = -0.673 - 3.622 \times 10^{-3}T + 3.048 \times 10^{-6}T^2 -$$
$$- 0.95 \times 10^{-9}T^3 + C_2(T)\, n + 139n^{-1}(n + 1)\, e^{-0.007T} \tag{1.55}$$

for n-alkynes

$$C_p^o = 2.965 - 21.514 \times 10^{-3}T + 11.779 \times 10^{-6}T^2 -$$
$$- 2.506 \times 10^{-9}T^3 + C_2(T)\, n + 5.657n^{-0.5}m^{-2} \times$$
$$\times (2.818 - 0.002T) \tag{1.56}$$

for n-alkylbenzenes

$$C_p^o = -8.356 - 112.72 \times 10^{-3}T - 71.306 \times 10^{-6}T^2 +$$
$$+ 16.93 \times 10^{-9}T^3 + C_2(T)\, z \tag{1.57}$$

for n-alkylcyclohexanes

$$C_p^o = -14.695 + 166.86 \times 10^{-3}T - 96.753 \times 10^{-6}T^2 +$$
$$+ 20.653 \times 10^{-9}T^3 + C_2(T)\, z - \{77.75T^{-2/3}\} \tag{1.58}$$

for saturated alcohols

$$C_p^\circ = -6.602 + 17.8 \times 10^{-3}T + 13.985 \times 10^{-6}T^2 -$$
$$- 12.51 \times 10^{-9}T^3 + C_2(T)\,n + \{242.2me^{-0.007T}\} \qquad (1.59)$$

for aldehydes

$$C_p^\circ = -6.882 + 5.98 \times 10^{-3}T + 21.188 \times 10^{-6}T^2 -$$
$$- 15.01 \times 10^{-9}T^3 + C_2(T)\,n + \{215\,(n^2 + m)^{-1}\,e^{-0.007T}\}$$
$$(1.60)$$

for acids

$$C_p^\circ = -5.692 + 18.2 \times 10^{-3}T + 12.248 \times 10^{-6}T^2 -$$
$$- 15.012 \times 10^{-9}T^3 + C_2(T)\,n + \{127.56n^{-1}m^{-1}e^{-0.007T}\}$$
$$(1.61)$$

for esters (methyl formate, etc.)

$$C_p^\circ = -14.54 + 24.2 \times 10^{-3}T + 27.58 \times 10^{-6}T^2 -$$
$$- 25.02 \times 10^{-9}T^3 + C_2(T)\,2n + \{14\,(10 - z)\,e^{-0.007T}\}$$
$$(1.62)$$

for mercaptanes $C_nH_{2n+1}SH$

$$C_p^\circ = -1.1583 + 8.272 \times 10^{-3}T - 1.597 \times 10^{-6}T^2 -$$
$$- 0.416 \times 10^{-9}T^3 + C_2(T)\,z \quad (\text{with } z \geqslant 4) \qquad (1.63)$$

for thioethers

$$C_p^\circ = -1.1583 + 8.272 \times 10^{-3}T - 1.597 \times 10^{-6}T^2 -$$
$$- 0.416 \times 10^{-9}T^3 + C_2(T)\,2z \quad (\text{with } z \geqslant 5) \qquad (1.64)$$

In Eq. (1.58), the term in braces is taken into account only for cyclohexane. The terms in braces in Eqs. (1.59) and (1.62) should be taken into account when calculating the heat capacities only for the first four, and in Eqs. (1.60) and (1.61) for the first five simplest compounds of each of the homologous series.

Equations (1.54) to (1.58) may be used to calculate the molar heat capacity within the interval from 250 to 1600 K with an average accuracy of from 0.2 to 0.5%. The accuracy is lower for the first three members of the series, however, and in some cases lowers to 1.5%, but for elevated temperatures it becomes equal to about 0.5%. Equations (1.59) to (1.62) are used to calculate the heat capacity within the interval from 298.15 to 1000 K, but with a considerably lower accuracy than in the other cases. Thus, for alcohols up to 600 K, the heat capacities found by Eq. (1.59) for the first two members of the series may differ from the true values by an average of 7.5 and 2%, respectively; for the remaining representatives of the normal alcohols, the accuracy of determining C_p°

ranges from 0.2 to 1.5 %. According to Eqs. (1.60) and (1.61), the accuracy of determining the heat capacities of aldehydes and acids for the first three or four representatives of the series up to 600 K is not over 2 to 7 % while for compounds with $n \geqslant 4$ the accuracy is of the order of magnitude of from 0.4 to 1 % throughout the entire interval from 298.15 to 1000 K (and it rapidly grows with increasing n). For ethers, the accuracy of determining C_p° for compounds with $n \geqslant 10$ is not over 0.5 to 1 %, and with $n < 10$ it is not over 2 to 10 %.

Example 34. Using Maslovs' method, derive equations for determining $(\Delta H_{298}^\circ)_{form}$ for (1) all the completely substituted halomethanes, and (2) partly substituted halomethanes.

Solution. 1. According to Eq. (1.47) for completely substituted halomethanes $CF_kCl_mBr_pI_q$, the standard heat of formation $(\Delta H_{298}^\circ)_{form}^g$ (for convenience the subscripts and superscript will be omitted in this example) can be expressed [50] as follows:

(a) $\Delta H_{CF_kCl_mBr_pI_q} = \frac{1}{4}(k\Delta H_{CF_4} + m\Delta H_{CCl_4} + p\Delta H_{CBr_4} + q\Delta H_{CI_4})$

where $n = k + m + p + q = 4$; $\delta_1 = k$; $\delta_2 = m$; $\delta_3 = p$; and $\delta_4 = q$.

Let us analyse Eq. (a). Assume that $k = 2$ and that the required compound contains no atoms of I, i.e. $q = 0$; hence, $m = p = 1$. In particular, for such halomethanes as CX_2YZ, CX_2Y_2, and CX_3Y where X, Y, and Z are halogens, Eq. (a) becomes

(b) $\Delta H_{CX_2YZ} = \frac{1}{4}(2\Delta H_{CX_4} + \Delta H_{CY_4} + \Delta H_{CZ_4})$

(c) $\Delta H_{CX_2Y_2} = \frac{1}{4}(2\Delta H_{CX_4} + 2\Delta H_{CY_4})$

(d) $\Delta H_{CX_3Y} = \frac{1}{4}(3\Delta H_{CX_4} + \Delta H_{CY_4})$

2. For partly substituted halomethanes in accordance with Eq. (1.47), the corresponding equations will be

(e) $\Delta H_{CH_2XY} = \frac{1}{2}(\Delta H_{CH_2X_2} + \Delta H_{CH_2Y_2})$

(f) $\Delta H_{CH_3X} = \frac{1}{2}(\Delta H_{CH_4} + \Delta H_{CH_2X_2})$

(g) $\Delta H_{CHXYZ} = \frac{1}{3}(\Delta H_{CHX_3} + \Delta H_{CHY_3} + \Delta H_{CHZ_3})$

Example 35. Find $(\Delta H_{298}^\circ)_{form}$ for gaseous $C_2Cl_2F_2$ if for gaseous C_2F_4 and C_2Cl_4 it equals [20] -151.3 and -3.6 kcal/mol, respectively. Use Maslovs' method.

Solution. For the given case, according to Eq. (1.47), an equation of the following kind can be used:

$$\Delta H_{C_2F_hCl_mBr_pI_q} = \frac{1}{4}\,(k\Delta H_{C_2F_4} + m\Delta H_{C_2Cl_4} + p\Delta H_{C_2Br_4} + q\Delta H_{C_2I_4})$$

For $C_2Cl_2F_2$ we have $p = 0$, $q = 0$, $k = 2$, and $m = 2$. Hence,

$$\Delta H_{C_2Cl_2F_2} = \frac{1}{4}\,(2\Delta H_{C_2F_4} + 2\Delta H_{C_2Cl_4})$$

Using this expression, we get the required value:

$$(\Delta H^\bullet_{298})_{form} = \frac{1}{4}\,[2\,(-151.3) + 2\,(-3.6)] = -77.5 \text{ kcal/mol}$$

According to published data [50], $(\Delta H^\circ_{298})_{form} = -76.0 \pm 2.0$ kcal/mol.

Example 36. Calculate $(\Delta H^\circ_{298})_{form}$ for gaseous C_2H_3Cl if its values for C_2H_4 and $C_2H_2Cl_2$ are 12.496 and 0.8 kcal/mol, respectively.

Solution. According to Eq. (1.47) recommended by P. Maslov and Yu. Maslov, we have

$$\Delta H_{C_2H_3Cl} = \frac{1}{2}\,(\Delta H_{C_2H_4} + \Delta H_{C_2H_2Cl_2})$$

Hence,

$$(\Delta H^\circ_{298})^g_{form} = \frac{1}{2}\,(12.496 + 0.8) = 6.64 \text{ kcal/mol}$$

The experimental value found in [50] is 7.00 kcal/mol.

1.3.10. Franklin's Method of Calculating $(\Delta H^\circ_{298})_{form}$. J. Franklin's method [46, 52] allows us to determine the heats of formation ΔH°_{form} and the Gibbs energy of formation ΔG°_{form} for hydrocarbons in the gaseous state. An advantage of this method in comparison with those considered above is the possibility of calculating ΔH°_{form} and ΔG°_{form} for any of a broad range of temperatures (from 0 to 1500 K). Franklin's method can be used for calculating the thermodynamic properties of various unsaturated, cyclic, and aromatic structures. The method cannot be used for halogen-, sulphur-, nitrogen-, and oxygen-containing compounds. The values of ΔH°_{form} obtained by this method coincide within the accuracy limits of ± 2 kcal/mol with experimentally found values for simple organic compounds and within the limits of ± 5 kcal/mol for complex compounds. Excep-

tions are dicyanogen, hydrazine, and acetic anhydride for which the method gives unsatisfactory results.

The calculations of the standard heats of formation are based on the assumption that ΔH°_{form} is an additive function of characteristic group constants. These constants are given in Appendix 9.

The method uses the relationship proposed by K. Pitzer [53] in which the heat capacity function $(H^{\circ}-H^{\circ}_0)/T$ is predicted theoretically for gaseous n-alkanes as an additive function of the number of carbon atoms in a molecule and of constants characterizing the temperature, stretching, deformation of the bonds, etc. To find the heat of formation of a molecule according to the values of $(H^{\circ} - H^{\circ}_0)/T$, we must know the heat of formation of the molecule at 0 K $[(\Delta H^{\circ}_0)_{form}]$:

$$(\Delta H^{\circ}_T)_{form} = (\Delta H^{\circ}_0)_{form} + (H^{\circ} - H^{\circ}_0) - \sum (H^{\circ} - H^{\circ}_0) \qquad (1.65)$$

<div align="center">(for com-   (for ele-
pounds)   ments)</div>

Using experimental values of ΔH°_{form} and calculated values of $(H^{\circ} - H^{\circ}_0)$ for a compound and for elements, Franklin showed that $(\Delta H^{\circ}_0)_{form}$ is an additive function and that the correction factors which he calculated can be used even for greatly branched molecules. Therefore, $(\Delta H^{\circ}_T)_{form}$ is also an additive function.

Franklin also used an additive method similar to that employed for calculating $(\Delta H^{\circ}_T)_{form}$ to compute the standard Gibbs energies of formation ΔG°_{form}. In calculations of the latter quantity, however, account must be taken of the intramolecular symmetry by adding to ΔG°_{form} the expression $R \ln \sigma$ (where R is the molar gas constant, cal/mol·K, and σ is the symmetry number of a molecule, i.e. the total number of identical orientations which a molecule can have upon rigid rotation about an axis or upon rotation inside the molecule; for instance, for methane $\sigma = 12$, for ethane $\sigma = 2$, for 1,3-butadiene $\sigma = 0$, for ethylamine $\sigma = 3$, and for isopropyl alcohol $\sigma = 1$).

In all the calculations, the value of σ is determined with the aid of the rule proposed by G. Herzberg [46, 54]. The discrepancies between the values of ΔH°_{form} calculated by Franklin's method and the experimentally found values usually range within the limits of ± 2 kcal/mol.

Example 37. Using Franklin's method, calculate $(\Delta H^{\circ}_{298})_{form}$ for gaseous ethylbenzene.

Solution. A molecule of ethylbenzene ⌬$-CH_2-CH_3$ has five groups of atoms $>CH$, one group $\vdots>C-$, one group $>CH_2$,

and one group — CH_3. In Appendix 9 we find the values of the contributions for the groups (in kcal/mol):

$$5 \quad {>}CH = 5 \times 3.30 = \quad 16.50$$

$$1 \quad {>}C- \qquad\qquad = \quad 5.57$$

$$1 \quad =CH_2 \qquad = \; -4.93$$

$$1 \quad -CH_3 \qquad = -10.12$$

$$(\Delta H^\circ_{298})_{form} \qquad = \quad 7.02$$

The experimentally found value is 7.12 kcal/mol [2].

Example 38. Using Franklin's method, calculate the standard heat of the reaction of alkylation of toluene with propylene proceeding in the gaseous phase at 25 °C.

Solution. We assume that the reaction proceeds as follows:
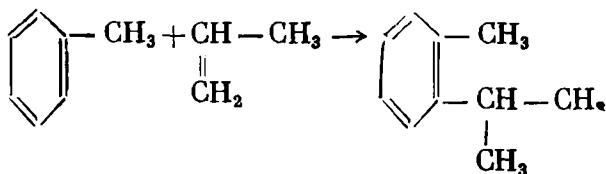
To determine the standard heat of the reaction ΔH°_{298}, we must know $(\Delta H^\circ_{298})_{form}$ for all the reagents. The values of this quantity for gaseous toluene and propylene are 11.950 and 4.879 kcal/mol, respectively (Appendix 1). Since these tables do not give the value of $(\Delta H^\circ_{298})_{form}$ for the product, we shall determine its value empirically using Franklin's method. In Appendix 9 we find the values of the group contributions for the molecule
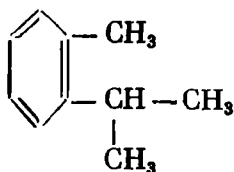
$$4 \text{ groups} \quad {>}CH = 4 \times 3.30 \qquad = \quad 13.2$$

$$2 \text{ groups} \quad {>}C- = 2 \times 5.57 \qquad = \quad 11.14$$

$$3 \text{ groups} \quad -CH_3 = 3\,(-10.12) \quad = -30.36$$

$$
\text{1 group} \quad -\overset{\displaystyle |}{\underset{\displaystyle |}{C}}H \qquad\qquad = \quad 12.04
$$

Correction for sub-
stitution of hydro-
gen in aromatic
nucleus 1,2 $=$ 0.6

$$(\Delta H^{\circ}_{298})_{form} \qquad = - \quad 6.62 \text{ kcal/mol}$$

Since we have neither an experimental nor a tabulated value of $(\Delta H^{\circ}_{298})_{form}$ for 1,2-isopropyltoluene, we shall compare $(\Delta H^{\circ}_{298})_{form}$ found by Franklin's method with its value found by some other empirical method. For example, we shall calculate the required thermodynamic property by the method of introducing corrections proposed by Anderson, Beyer, and Watson (Appendix 7).

$$(\Delta H^{\circ}_{298})_{form} \ 19.82 \qquad -7.87 \qquad\qquad -7.41$$
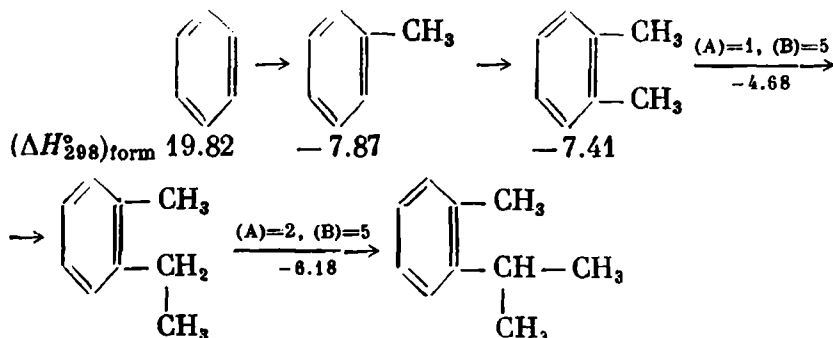
Thus, the required value is

$$(\Delta H^{\circ}_{298})_{form} = 19.82 - 7.87 - 7.41 - 4.68 - 6.18 = -6.32 \ \text{kcal/mol}$$

Comparison of the values of $(\Delta H^{\circ}_{298})_{form}$ found by using two different empirical methods gives a very good convergence.

The corollary of Hess's law permits us to find the heat of the reaction:

$$\Delta H^{\circ}_{298} = -6.62 - (11.950 + 4.879) = -23.449 \ \text{kcal}$$

1.3.11. Souders's, Matthews's, and Hurd's Method of Calculating $(\Delta H^{\circ}_{298})_{form}$. M. Souders, C. Matthews, and C. Hurd [46, 55] proposed an additive method of determining $(\Delta H^{\circ}_{298})_{form}$ and the true molar heat capacities C°_p at constant pressure within a broad range of temperatures (from 300 to 2000 K) for hydrocarbons in the gaseous state. A merit of the method is that the appropriate corrections can be used to take into account the influence of definite neighbouring groups. The discrepancy between the values of $(\Delta H^{\circ}_{298})_{form}$ calculated according to this method and the experimental ones does not usually exceed from 0.5 to 1 kcal/mol.

To calculate the standard heat of formation of hydrocarbons at any temperature $(\Delta H_T^\circ)_{\text{form}}$, Souders et al used the Kirchhoff equation (1.88) which, for the case of separation of the different kinds of energy in the expression for the heat capacities, has the form

$$(\Delta H_T^\circ)_{\text{form}} = (\Delta H_{298}^\circ)_{\text{form}} + \left[\int_{298}^{T} C_{p(\text{vib})}^\circ \, dT - \right.$$

$$- \frac{n}{2} \int_{298}^{T} C_{p(\text{H}_2)}^\circ \, dT - m \int_{298}^{T} C_{p(\text{gr})}^\circ \, dT \bigg]_{\text{I}} +$$

$$+ \left[\int_{298}^{T} C_{p(\text{int. rot})}^\circ \, dT \right]_{\text{II}} + 4R \, (T - 298) \qquad (1.66)$$

where the value of $(\Delta H_{298}^\circ)_{\text{form}}$ for the required hydrocarbon is determined by summation of the group contributions given in Appendix 10a; $C_{p(\text{H}_2)}^\circ$ and $C_{p(\text{gr})}^\circ$ are the heat capacities of hydrogen and solid graphite in standard conditions; n and m are the numbers of hydrogen and carbon atoms in an atomic group; $C_{p(\text{vib})}^\circ$ is the vibrational component of the heat capacity; and $C_{p(\text{int.rot})}^\circ$ is the component of the heat capacity due to internal rotation.

The integrals I and II in Eq.(1.66) were verified for various atomic groups and bonds of hydrocarbons; their values are given in Appendices 10b and 10c. The quantity $4R(T - 298)$ is the change in the enthalpy with the temperature due to the components of translational motion, external rotation, and also takes into account the difference $C_p - C_V = R$.

Example 39. Calculate $(\Delta H_{298}^\circ)_{\text{form}}$ for gaseous methylacetylene using the method of Souders et al.
Solution. Methylacetylene $CH_3—C\equiv CH$ can be divided into three groups: $H —C\equiv$, $—C\equiv$, and $—CH_3$. From Appendix 10a, the contributions of these groups have the values

$$H — C \equiv \qquad 27.04$$
$$— C \equiv \qquad 27.65$$
$$— CH_3 \qquad — 10.05$$

$(\Delta H_{298}^\circ)_{\text{form}} = 44.4$ kcal/mol

The experimental value [20] is 44.32 kcal/mol.

Example 40. Determine $(\Delta H_{800}^\circ)_{\text{form}}$ for gaseous 2-butene *(trans)* at 800 K using the method of Souders et al.
Solution. 2-Butene $CH_3—CH=CH—CH_3$ can be divided into two $—CH_3$ groups and two $—HC=$ *(trans)* groups.

We find $(\Delta H^\circ_{298})_{form}$ with the aid of Appendix 10a:

$$2(-CH_3) \quad = 2(-10.05) = -20.10$$
$$2(-HC=) = 2 \times 8.70 \quad = \quad 17.40$$

$$\overline{(\Delta H^\circ_{298})_{form} \qquad\qquad = -2.70 \text{ kcal/mol}}$$

Using Appendix 10b, we determine integral I in Eq. (1.66) for 800 K:

$$2(-CH_3) \quad = 2(-4.594) = \quad -9.19$$
$$2(-HC=) = 2(-0.853) = \quad -1.71$$

$$\overline{\qquad\qquad\qquad\qquad -10.90 \text{ kcal/mol}}$$

We find integral II in Eq. (1.66) in Appendix 10c and include the contributions for two bonds of the type —HC= (*trans*):

$$2(0.554) = 1.11 \text{ kcal/mol}$$

We find the quantity $4R\,(T - 298) = 4 \times 1.987\,(800 - 298) = 3.99$ kcal/mol.

The standard heat of formation of 2-butene at 800 K equals the sum of the found values:

$$(\Delta H^\circ_{800})_{form} = -2.70 - 10.90 + 1.11 + 3.99 = -8.50 \text{ kcal/mol}$$

The experimentally found value is —7.89 kcal/mol [46].

1.4
Heat Capacity

1.4.1. Definitions. Heat Capacity in Various Processes. Relationship Between C_p and C_V. By *heat capacity* is meant the quantity of heat which must be spent to raise the temperature of a unit of mass of a substance by one kelvin. The heat capacity of all substances depends on the temperature; therefore, the true and the mean heat capacities are distinguished. By the *true heat capacity* C at a temperature t is meant the heat capacity of a system at this temperature:

$$C = \frac{\delta Q}{dt} \tag{1.67}$$

The *mean heat capacity* $\bar{C}$ is a constant quantity within the temperature interval from t_1 to t_2; it equals

$$\bar{C} = \frac{Q}{t_2 - t_1} \tag{1.68}$$

where Q is the amount of heat needed to heat the system from t_1 to t_2.

The heat capacity related to a unit of mass of a substance, for example to one kilogram or one gramme, is called the *specific heat capacity*. The heat capacity related to one mole or one gramme-atom is called the *molar* or the *atomic heat capacity*, respectively. Heat is most often measured in calories; therefore, the specific heat capacity is measured in cal/g·K, and the molar heat capacity in cal/mol·K. Since the basic unit of energy in the International System of Units (SI) is the joule, the specific and molar heat capacities are quite often expressed in J/g·K and J/mol·K, respectively.

The heat capacity of a definite thermodynamic system depends on the nature of a process. For instance, if we consider the heat capacity of a system in an isochoric, isobaric, or adiabatic process, in the first two processes $\bar{C}$ has a finite value because when $Q \neq 0$ we also have $(t_2 - t_1) \neq 0$, whereas in an adiabatic process we have $\bar{C} = 0$ because $Q = 0$ while $(t_2 - t_1) \neq 0$.

In isothermal processes with the supply of heat to a system or the removal of heat from it, the heat capacity of the system equals either $+\infty$ or $-\infty$, respectively, because in accordance with the definition of an isothermal process, the change in temperature equals zero.

For the heat capacity of a system being considered to have a definite value, it is necessary to accurately indicate the kind of process it relates to. Depending on the conditions of a process, we can consider different kinds of heat capacities of the same thermodynamic system. Only a very small number of these heat capacities, however, are of practical importance. Most frequently, the isochoric and isobaric heat capacities C_V and C_p or, as they are often called, the heat capacity at constant volume and the heat capacity at constant pressure are used in chemical thermodynamics.

In Eq. (1.67), δQ is an infinitely small quantity which in the general case is not a total differential. This means that Q and, consequently, $\bar{C}$ (like the quantities δQ and C) in the general case depend on the path followed in heating the system from t_1 to t_2. In other words, for many processes the heat capacity of a thermodynamic system characterizes not only its properties, but also the heating process itself. For processes at $p = $ const or $V = $ const, the quantity Q is a total differential, and the heat capacity does not depend on how the system passes from the state with the temperature t_1 to that with the temperature t_2. In an isochoric process, $Q_V = \Delta U$ and $dQ_V = dU$. Hence, it follows that at $V = $ const the mean heat capacity

$$\bar{C}_V = \frac{\Delta U}{t_2 - t_1} \qquad (1.69)$$

and the true heat capacity

$$C_V = \left(\frac{\partial U}{\partial t} \right)_V \qquad (1.70)$$

In an isobaric process, $Q_p = \Delta H$ and $dQ_p = dH$. Thus, the mean $\overline{C}_p$ and the true C_p heat capacities at $p = \text{const}$ are determined by the equations

$$\overline{C}_p = \frac{\Delta H}{t_2 - t_1} \tag{1.71}$$

and

$$C_p = \left(\frac{\partial H}{\partial t}\right)_p \tag{1.72}$$

The heat capacity at constant pressure is always greater than that at constant volume. The difference between these two quantities $(C_p - C_V)$ equals the work of expansion of a system when the temperature changes by one kelvin done as a result of the supply of additional heat.

The relationship between C_p and C_V can be easily found from the first law of thermodynamics

$$C_p - C_V = l \left(\frac{\partial V}{\partial T}\right)_p \tag{1.73}$$

The quantity l in this expression is a caloric coefficient which in accordance, with the general laws of thermodynamics is determined as

$$l = T \left(\frac{\partial p}{\partial T}\right)_V$$

In this case

$$C_p - C_V = T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \tag{1.74}$$

For one mole of an ideal gas

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \quad \text{and} \quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$$
$$C_p - C_V = R \tag{1.75}$$

For more accurate calculation of the derivatives $(\partial p/\partial T)_V$ and $(\partial V/\partial T)_p$ when dealing with non-ideal gases, it is necessary to use experimental data on the temperature dependence of the pressure and volume of a gas. When insufficient data are available for calculating the derivatives, equations of state for non-ideal (real) gases may be used, for instance the van der Waals equation. In this case for pressures not too high and temperatures not too low, the relationship between C_p and C_V will be expressed as follows [12]:

$$C_p - C_V = R \left(1 + \frac{2a}{R^2 T^2} p\right) \tag{1.76}$$

where a is a constant of the van der Waals equation.

Since a is a positive quantity, the value of $(C_p - C_V)$ for non-ideal gases is somewhat greater than R. This difference grows with increasing pressure or decreasing temperature.

1.4.2. Temperature Dependence of Heat Capacity. Relationship Between Mean and True Heat Capacities. Heat capacity depends greatly on temperature. This dependence cannot be established through other properties of a substance on the basis of the laws of thermodynamics. It is studied experimentally or calculated by methods of quantum statistical physics. The temperature dependence of heat capacity found in one way or another is expressed by empirical power series. Generally such a relationship for a preset temperature interval is given for the heat capacity determined at constant pressure. For example, the temperature dependence of the true and mean molar heat capacities at constant pressure can be written as follows (respectively):

$$C_p = a' + b't + c't^2 + d't^3 + \ldots \tag{1.77}$$

and

$$\overline{C}_p = \alpha' + \beta't + \gamma't^2 + \delta't^3 + \ldots \tag{1.78}$$

where a', b', c', d' ... and α', β', γ', δ' ... are coefficients of the temperature dependence of the heat capacity characteristic of a given substance.

The number of terms in Eqs. (1.77) and (1.78) depends on the required degree of accuracy and on the temperature interval. Usually three-term series of $C_p = \varphi(t)$ are used in practical calculations. The coefficients a', b', and c' are found on the basis of experimental or calculated data with the aid of the rule of least squares. It should be borne in mind that the coefficient a' in Eq. (1.77) is not the heat capacity of a substance at $t = 0$ °C.

Most of the relationships $C_p = \varphi(t)$ available at present for gases have been found on the basis of spectral data. Therefore, they relate to the condition $p \to 0$, i.e. to the ideal gaseous state, and as applied to it are distinguished for their high accuracy. At $p = 1$, the difference between $C_{p=0}$ and $C_{p=1}$ becomes significant only at a low temperature while at a high one it forms fractions of a per cent. With a certain approximation, an equation $C_p = \varphi(t)$ may also be used for moderate pressures (remote from saturation even up to $p = 5$-10 atm). For a high pressure, its influence on the heat capacity must already be taken into consideration.

The heat capacity of gases at any temperature can be determined with the aid of the kinetic theory of gases or the Planck-Einstein quantum theory of heat capacities. According to the kinetic theory of gases, the true molar heat capacity at constant volume for mon-

atomic gases

$$C_V = \frac{3}{2} R = \text{const}$$

For polyatomic gases, C_V changes with the temperature because in the general case

$$C_V = C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}} + C_{\text{el}} \tag{1.79}$$

where C_{trans}, C_{rot}, and C_{vib} are the addends of the heat capacity for translational, rotational, and vibrational motion of the molecules of any gas, respectively (for any gas $C_{\text{trans}} = 3R/2$); C_{el} is an addend of the heat capacity taking into account electron excitation.

Since the energy of rotational motion of the molecules of all gases except hydrogen and deuterium reaches its maximum value at a moderate temperature, C_{rot} is calculated following the principle of equal distribution of the energy by degrees of freedom. Hence, for diatomic and polyatomic gases with linear molecules, $C_{\text{rot}} = 2R/2$ while for triatomic and polyatomic gases $C_{\text{rot}} = 3R/2$. The vibrational addend of the heat capacity of a gas per degree of freedom, according to the Planck-Einstein quantum theory of heat capacities, is determined by the equation

$$C_{\text{vib}} = \left(\frac{\Theta}{T}\right)^2 \frac{Re^{\Theta/T}}{(e^{\Theta/T} - 1)^2} = \psi\left(\frac{\Theta}{T}\right) \tag{1.80}$$

The only constant in this equation characterizing an individual gas is the characteristic temperature $\Theta = h\nu_0/k$ (where h is the Planck constant, ν_0 is the frequency of natural vibrations of a molecule, and k is the Boltzmann constant), and the only variable is the ratio Θ/T. The last addend in Eq. (1.79), C_{el}, may be omitted because electron excitation needs a very high temperature. As a result, we get (if the pressure is not great)

$$C_p = C_V + R = \frac{3}{2} R + \frac{n}{2} R + R +$$

$$+ \sum^{3m-(3+n)} \left(\frac{\Theta}{T}\right)^2 \frac{Re^{\Theta/T}}{(e^{\Theta/T} - 1)^2} = \frac{5+n}{2} R + \sum \psi\left(\frac{\Theta}{T}\right) \tag{1.81}$$

where n = number of rotational degrees of freedom
m = total number of atoms in a molecule.

For gases with a linear structure (diatomic gases, CO_2, COS, HCN, C_2H_2, CS_2, etc.), the number of degrees of freedom of the vibrational addend of the heat capacity C_{vib} equals

$$3m - (3 + 2) = 3m - 5$$

for other polyatomic gases it equals

$$3m - (3 + 3) = 3m - 6$$

The last addend of the right-hand side of Eq. (1.81) is calculated with the aid of tables of the Einstein functions.

The characteristic temperatures Θ for selected gases and the Einstein functions are given in Appendices 11 and 12, respectively.

If we know an expression for the temperature dependence of C_p or $\overline{C}_p$, it is a simple matter to calculate the mean heat capacity from the true one and vice versa.

Assume that for the interval from 0 to t °C, the mean heat capacity is given as a function of temperature in the form of the power series

$$\overline{C}_p = \alpha' + \beta' t + \gamma' t^2 + \ldots$$

It follows from Eq. (1.68) that at $t = 0$ °C and $p = $ const, we have

$$\overline{C}_p = \frac{\Delta H}{t}$$

$$\Delta H = \alpha' t + \beta' t^2 + \gamma' t^3 + \ldots$$

But the true heat capacity according to Eq. (1.67) is

$$C_p = \left(\frac{\partial H}{\partial t} \right)_p = \left\{ \frac{\partial (\overline{C}_p t)}{\partial t} \right\}_p^{*} \tag{1.82}$$

Hence,

$$C_p = \left(\frac{\partial H}{\partial t} \right)_p = \alpha' + 2\beta' t + 3\gamma' t^2 + \ldots \tag{1.83}$$

Assume that the true molar heat capacity at $p = $ const is given in the form of a series [see Eq. (1.83)] and it is necessary to determine the mean molar heat capacity $\overline{C}_p$ within the temperature interval from t_1 to t_2. According to Eq. (1.71), ΔH can be calculated from Eq. (1.83):

$$\Delta H = \int_{t_1}^{t_2} C_p \, dt = \int_{t_1}^{t_2} (\alpha' + 2\beta' t + 3\gamma' t^2 + \ldots) \, dt$$

Hence,

$$\overline{C}_p = \frac{\Delta H}{t_2 - t_1} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} C_p \, dt =$$

$$= \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} (\alpha' + 2\beta' t + 3\gamma' t^2 + \ldots) \, dt =$$

$$= \frac{1}{t_2 - t_1} [\alpha' (t_2 - t_1) + \beta' (t_2^2 - t_1^2) + \gamma' (t_2^3 - t_1^3) + \ldots] =$$

$$= \alpha' + \beta' (t_2 + t_1) + \gamma' (t_2^2 + t_2 t_1 + t_1^2) + \ldots \tag{1.84}$$

---

* Since $H = \int_0^t \overline{C}_p \, dt + H_0 = \overline{C}_p \int_0^t dt + H_0 = \overline{C}_p t + H_0.$

Usually the true molar heat capacity at constant pressure is given as a function of the absolute temperature. In this case, introducing $t = T - 273.15$ into Eq. (1.77) and combining free terms, we get the power series

$$C_p = a + bT + cT^2 + \ldots \tag{1.85}$$

It is exactly the relationship $C_p = f(T)$ that we shall use in our further calculations.

Example 41. Calculate C_V for methane at 25 °C if at the same temperature and at $p=1$ atm we have $C^\circ_{p,\,298} = 8.536$ cal/mol·K [20]. Consider that (a) methane is an ideal gas; and (b) it is a gas obeying the van der Waals equation.

Solution. If methane is considered as an ideal gas, then according to Eq. (1.75) we have $C_V = C_p - R$, or

$$C_V = 8.536 - 1.987 = 6.549 \quad \text{cal/mol·K}$$

If we consider that methane obeys the van de Waals equation, then according to Eq. (1.76) we have

$$C_V = C_p - R \left(1 + \frac{2a}{R^2 T^2}\, p \right)$$

The van der Waals constant $a = 0.004\ 49$ cm^6·atm/mol^2 [7]. Since 1 cm^3·atm $= 0.0242$ cal, we get

$$C_V = 8.536 - 1.987 \left(1 + \frac{2 \times 0.004\ 49 \times 0.0242}{1.987^2 \times 298.15^2} \right) =$$

$$= 8.536 - 1.987 \,(1 + 0.6 \times 10^{-9}) = 6.549 \quad \text{cal/mol·K}$$

A glance at the results of the calculations shows that the correction for the deviation of the non-ideal system from an ideal one is so small that it may be ignored, and methane may be considered as an ideal gas in the given conditions.

Example 42. Find C°_p for methane through every 200 kelvins within the interval from 300 to 1500 K using the equation of the Planck-Einstein theory of quantum heat capacity.

Solution. By Eq. (1.81)

$$C_p = 7.949 + \sum \psi \left(\frac{\Theta}{T} \right)$$

We use Appendix 11 to find the characteristic temperatures Θ corresponding to methane at the required temperatures T. Next, using Appendix 12, we calculate the vibrational components of the heat capacities C_{vib} for the required temperatures according to the

found values of Θ/T:

$$\Theta \qquad . \ . \qquad 1870 \times (3) \qquad 2170 \times (2) \qquad 4320 \times (3) \qquad 4400$$

$T = 300$ K: $\dfrac{\Theta}{T}$ . . $\qquad 6.233 \qquad 7.233 \qquad 14.400 \qquad 14.667$

C_{vib}° . . $3 \times 0.154 + 2 \times 0.075 + 3 \times 0.000 + 0.000 = 0.812$

$T = 500$ K: $\dfrac{\Theta}{T}$ . . $\qquad 3.740 \qquad 4.340 \qquad 8.640 \qquad 8.800$

C_{vib}° . . $3 \times 0.693 + 2 \times 0.501 + 3 \times 0.027 + 0.023 = 3.185$

$T = 700$ K: $\dfrac{\Theta}{T}$ . . $\qquad 2.671 \qquad 3.100 \qquad 6.171 \qquad 6.286$

C_{vib}° . . $3 \times 1.132 + 2 \times 0.943 + 3 \times 0.160 + 0.148 = 5.590$

$T = 900$ K: $\dfrac{\Theta}{T}$ . . $\qquad 2.078 \qquad 2.522 \qquad 4.800 \qquad 4.889$

C_{vib}° . . $3 \times 1.403 + 2 \times 1.201 + 3 \times 0.383 + 0.361 = 8.121$

$T = 1100$ K: $\dfrac{\Theta}{T}$ . . $\qquad 1.700 \qquad 1.973 \qquad 3.927 \qquad 4.000$

C_{vib}° . . $3 \times 1.570 + 2 \times 1.452 + 3 \times 0.628 + 0.604 = 10.102$

$T = 1300$ K: $\dfrac{\Theta}{T}$ . . $\qquad 1.438 \qquad 1.670 \qquad 3.323 \qquad 3.384$

C_{vib}° . . $3 \times 1.678 + 2 \times 1.584 + 3 \times 0.851 + 0.826 = 11.581$

$T = 1500$ K: $\dfrac{\Theta}{T}$ . . $\qquad 1.247 \qquad 1.446 \qquad 2.880 \qquad 2.933$

C_{vib}° . . $3 \times 1.748 + 2 \times 1.675 + 3 \times 1.039 + 1.016 = 12.727$

The heat capacity in its final form at various temperatures (in cal/mol·K) is given below:

T, K . . .	300	500	700	900	1100	1300	1500
C_p°	8.761	11.134	13.539	16.070	18.051	19.530	20.776

A comparison of the results obtained with experimental data [19] gives a deviation less than 0.2 % for the region of low temperatures, where the values of C_p° calculated according to experimental data are the most reliable.

Example 43. The temperature dependence of the molar heat capacity of acetylene at $p = 1$ atm is expressed by the following experimental data [9]:

T, K	300	400	500	600	700	800	900	1000
C_p°, cal/mol·K	9.91	11.07	12.13	13.04	13.82	14.51	15.10	15.63

Use the method of least squares to compile an equation $C_p = \varphi(T)$ of the form corresponding to Eq. (1.77). Verify the accuracy of the compiled equation.

Solution. Before commencing to solve this example, let us remind ourselves of the basic propositions of the method of least squares. Assume that we have a series of pairs of values which in tabulated form express the dependence of one quantity (y) on the other (x), for example, as in our case, of the heat capacity on the temperature. It is necessary to find such numerical values of the coefficients in the equation

$$y = f(x) = a + bx + cx^2 + \ldots$$

that will satisfy in the best possible way the tabulated data. The problem should be solved so that the value of y calculated by the compiled equation at the given value of x should on an average be the closest possible to the actually found value. This condition is assumed to be observed when the sum of the squares of the differences between each two corresponding values of the quantities of both series (calculated and found experimentally) is minimum:

$$\sum (y_{exp} - a - bx - cx^2)^2 = \min$$

and this can occur only if the partial derivatives of the sum of the squares of the discrepancies with respect to a, b, and c equal zero:

$$\frac{\partial \sum (y - a - bx - cx^2)^2}{\partial a} = -2 \sum (y - a - bx - cx^2) = 0$$

$$\frac{\partial \sum (y - a - bx - cx^2)^2}{\partial b} = -2 \sum [x(y - a - bx - cx^2)] = 0$$

$$\frac{\partial \sum (y - a - bx - cx^2)^2}{\partial c} = -2 \sum [x^2(y - a - bx - cx^2)] = 0$$

After dividing by -2, we get

$$\sum (y - a - bx - cx^2) = 0$$

$$\sum [x(y - a - bx - cx^2)] = 0$$

$$\sum [x^2(y - a - bx - cx^2)] = 0$$

If the number of measurements is n, then $\sum a = na$. The last three equations now become

(1) $\sum y = na + b \sum x + c \sum x^2$

(2) $\sum xy = a \sum x + b \sum x^2 + c \sum x^3$

(3) $\sum x^2 y = a \sum x^2 + b \sum x^3 + c \sum x^4$

For simplifying our calculations, we shall introduce the following notation:

(4) $y = C_p$

(5) $x = \dfrac{T - 300}{100}$

(6) $y = a + bx + cx^2$

1. The calculations consist in finding the coefficients a, b, and c in the sixth equation by solving the system including the first, second, and third equations. We tabulate the values of y, x, x^2, x^3, x^4, xy, and x^2y needed for the calculations:

T	$y = C_p$	x	x^2	x^3	x^4	xy	x^2y
300	9.91	0	0	0	0	0	0
400	11.07	1	1	1	1	11.07	11.07
500	12.13	2	4	8	16	24.26	48.52
600	13.04	3	9	27	81	39.12	117.36
700	13.82	4	16	64	256	55.28	221.12
800	14.51	5	25	125	625	72.55	362.75
900	15.10	6	36	216	1296	90.60	543.60
1000	16.63	7	49	343	2401	109.41	765.87
Total	105.21	28	140	784	4676	402.29	2070.29

We compile a system of equations:

(7) $105.21 = 8a + 28b + 140c$

(8) $402.29 = 28a + 140b + 784c$

(9) $2070.29 = 140a + 784b + 4676c$

We exclude a from Eqs. (7) and (8). For this purpose we multiply Eq. (7) by -7 and Eq. (8) by 2:

(10) $-736.47 = -56a - 196b - 980c$

(11) $804.58 = 56a + 280b + 1568c$

After summing the last two equations, we get

(12) $68.11 = 84b + 588c$

We multiply Eq. (7) by -35, Eq. (9) by 2 and get

(13) $-3682.35 = -280a - 980b - 4900c$

(14) $4140.78 = 280a + 1568b + 9352c$

After summing the equations obtained, we have

(15) $458.43 = 588b + 4452c$

Multiplying Eq. (12) by 7 and subtracting Eq. (15) from it, we find the value of c:

$$\begin{array}{r} 476.77 = 588b + 4116c \\ - \underline{458.43 = 588b + 4452c} \\ 18.34 = -336c \end{array} \quad c = -\frac{18.34}{336} = -0.0542$$

We insert the value of c in Eq. (12) and calculate b:

$$b = \frac{68.11 + 588 \times 0.0542}{84} = 1.19$$

After introducing the found values of b and c in Eq. (7), we finally determine the coefficient a:

$$a = \frac{105.21 + 0.0542 \times 140 - 28 \times 1.19}{8} = 9.9347$$

Hence,

(16) $y = 9.9347 + 1.19x - 0.0542x^2$

Using in Eq. (16) instead of y and x their values from Eqs. (4) and (5), we have

$$C_p = 9.9347 + 1.19\frac{T-300}{100} - 0.0542\left(\frac{T-300}{100}\right)^2$$

After transformation, we get

$$C_p = 5.88 + 0.015\,15T - 0.000\,005\,42T^2$$

2. Below we compare the experimental values of C_p with those calculated by the found equation:

T, K	300	400	500	600	700	800	900	1000
$C_{p\,(exp)}$	9.91	11.07	12.13	13.04	13.82	14.51	15.10	15.63
$C_{p\,(calc)}$	9.93	11.07	12.10	13.02	13.83	14.53	15.12	15.60

The discrepancies do not exceed 0.25%.

Example 44. The mean molar heat capacity of CH_4 at constant volume within the interval from 298 to 1500 K is given by the expression

$$\overline{C}_V = 8.983 + 30.229 \times 10^{-3}T + 3.723 \times 10^{-7}T^2 \text{ J/mol} \cdot \text{K}$$

Find the true molar heat capacity of methane at constant pressure and 25 °C.

Solution. Considering that methane obeys the laws of ideal gases, we use Eq. (1.75) to find an expression for the mean value of the molar heat capacity of CH_4 at constant pressure:

$$\bar{C}_p = 8.31 + 8.983 + 30.229 \times 10^{-3}T + 3.723 \times 10^{-7}T^2$$

where $R = 8.31$ J/mol·K. But from Eq. (1.82), it follows that

$$C_p = \frac{d(\bar{C}_p T)}{dT} = \frac{d}{dT}(17.297T + 30.229 \times 10^{-3}T^2 +$$

$$+ 3.723 \times 10^{-7}T^3) = 17.297 + 60.458 \times 10^{-3}T + 11.169 \times 10^{-7}T^2$$

For 298 K

$$C_p = 17.297 + 60.458 \times 10^{-3} \times 298 + 11.169 \times 10^{-7} \times 298^2 =$$

$$= 36.305 \text{ J/mol·K} = 8.675 \text{ cal/mol·K}$$

Example 45. The value of C_p for gaseous 1,3-butadiene within the interval from 298 to 1500 K is given by the equation

$$C_p = -0.707 + 81.282 \times 10^{-3}T - 53.463 \times 10^{-6}T^2 \text{ cal/mol·K}$$

Determine $\bar{C}_p$ for the interval from 400 to 500 K.
Solution. According to Eq. (1.84)

$$\bar{C}_p = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} C_p \, dT$$

we have

$$\bar{C}_p = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} (-0.707 + 81.282 \times 10^{-3}T -$$

$$- 53.463 \times 10^{-6}T^2) \, dT = -0.707 + 40.641 \times 10^{-3}(T_2 + T_1) -$$

$$- 17.821 \times 10^{-6}(T_2^2 + T_2T_1 + T_1^2) = -0.707 + 40.641 \times$$

$$\times 10^{-3}(400 + 500) - 17.821 \times 10^{-6}(400^2 + 400 \times 500 + 500^2) =$$

$$= 25.149 \text{ cal/mol·K}$$

1.4.3. Some Empirical Methods of Calculating the Standard Heat Capacity C_p° of Gaseous Organic Substances. The method of calculating the heat capacities of gases using the Planck-Einstein quantum theory of heat capacities considered above allows us to calculate the heat capacity of simple gases (mainly monoatomic and diatomic, but sometimes also polyatomic). In most cases, however, accurate calculations are impossible for polyatomic molecules, and theory permits us to perform only approximate calculations. In these cases, the experimental value of the heat capacity obtained by reliable calorimetric methods should naturally be preferred to the calculated values.

At present a large amount of sufficiently dependable experimental data are available on the heat capacity of organic substances. These data are tabulated. Reference books usually give the standard true molar heat capacity at 25 °C ($C_{p,\,298}^{\circ}$) or its temperature dependence in the form of the power series

$$C_p^{\circ} = a + bT + cT^2$$

the recommended temperature interval for the given series being indicated.

The most complete summary of $C_{p,\,298}^{\circ}$ for a variety of compounds can be found in fundamental reference books [1-3, 5, 7-9, 16-33, 56]. Values of $C_{p,\,298}^{\circ}$ and the coefficients a, b, and c of the relationship $C_p^{\circ} = \varphi\,(T)$ for selected simple substances, inorganic and organic compounds are also given in Appendix 1 of the present book.

In the absence of experimental or calculated data in the cited reference books, the heat capacity of an organic compound being considered in the gaseous state can be assessed by empirical methods. From among the great number of empirical methods of calculating the heat capacity available at present, we can recommend the following methods of calculating thermodynamic quantities which have been considered on earlier pages: the method of Anderson, Beyer, and Watson, Maslovs' method, the method of Souders, Matthews, and Hurd.

Example 46. Using the method of introducing corrections for the substitution of hydrogen by —CH₃ groups, find the temperature dependence of C_p° for gaseous dichloroethyne.

Solution. We represent the structure of a molecule of dichloroethyne Cl —C ≡ C — Cl in the form of the following scheme, taking the required data from Appendix 7:

		(B)	(A)	(A)=1, (B)=1
	CH₄	⟶	CH₃ — CH₃	⟶
a	3.79	—2.00	0.49	
$b \times 10^3$	16.62	23.20	22.04	
$c \times 10^6$	—3.24	—9.12	—8.96	

	(B)	(A)	(A)=1, (B)=2	(A)	(B)
→ CH₃ — CH₂ — CH₃	⟶	CH₃ — CH₂ — CH₂ — CH₃ →			
		1.09			
		17.79			
		—6.47			

$$\xrightarrow[\text{(A)=2, (B)=2}]{} CH_3 - C \equiv C - CH_3 \longrightarrow Cl - C \equiv C - CH_3 \rightarrow$$

1.00	2.19
−25.70	−18.85
−9.50	6.26

$$\longrightarrow Cl - C \equiv C - Cl$$

2.19
−18.85
6.26
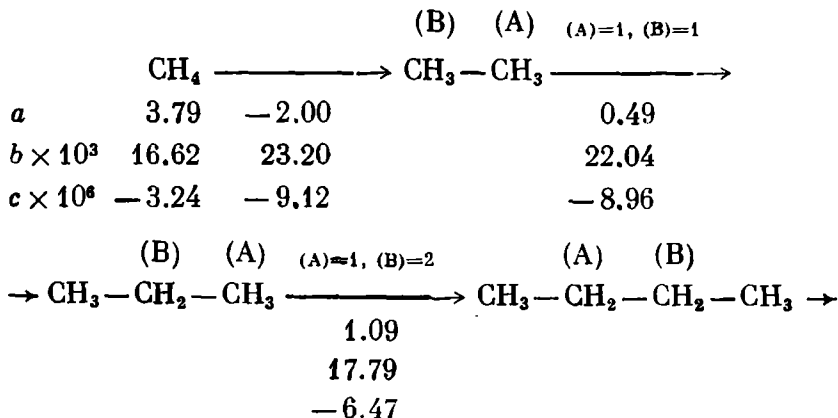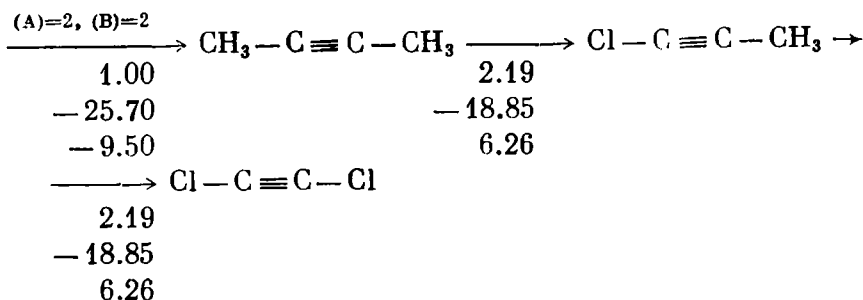
Summating all the corrections, we get the required relationship:

$$C_p^\circ = -8.75 + 16.35 \times 10^{-3}T - 26.77 \times 10^{-6}T^2$$

Example 47. Use Maslovs' method to find $C_{p,2\,98}^\circ$ for gaseous CFCl$_3$ if for CF$_4$ and CCl$_4$ it equals 14.61 and 19.96 cal/mol·K, respectively [20].

Solution. According to Eq. (1.46)

$$C_{p\,CFCl_3}^\circ = \frac{1}{4}(C_{p\,CF_4}^\circ + 3C_{p\,CCl_4}^\circ) =$$
$$= \frac{1}{4}(14.61 + 3 \times 19.96) = 18.59 \text{ cal/mol·K}$$

The experimentally found value [20] is 18.59.

Example 48. Find the true molar heat capacity of ethylbenzene at a constant pressure of 1 atm in the state of an ideal gas at 25 °C. Use Maslovs' method in the calculations.

Solution. For *n*-alkylbenzenes, C_p° within the interval from 250 to 1600 K is calculated by Maslovs' formula (1.57):

$$C_p^\circ = -8.356 + 112.72 \times 10^{-3}T - 71.306 \times 10^{-6}T^2 +$$
$$+ 16.93 \times 10^{-9}T^3 + C_2(T)\,z$$

But $C_2(T)$, according to Eq. (1.53), equals

$$C_2(T) = 0.1203 + 21.3 \times 10^{-3}T - 11.633 \times 10^{-6}T^2 +$$
$$+ 2.502 \times 10^{-9}T^3$$

Hence, taking into account that for ethylbenzene $z = 2$ (two methyl groups in the linear hydrocarbon chain), we have

$$C_p^\circ = -8.356 + 112.72 \times 10^{-3}T - 71.306 \times 10^{-6}T^2 +$$
$$+ 16.93 \times 10^{-9}T^3 + 2(0.1203 + 21.3 \times 10^{-3}T - 11.633 \times$$
$$\times 10^{-6}T^2 + 2.502 \times 10^{-9}T^3) = -8.115 + 155.32 \times 10^{-3}T -$$
$$- 94.572 \times 10^{-6}T^2 + 21.934 \times 10^{-9}T^3$$

At 298.15 K, we have $C_p^\circ = 30.16$ cal/mol·K. The experimental value according to M. Karapetyants [20] is 30.69.

I.5

Temperature Dependence of the Heat of a Reaction

Knowing the standard heat of formation or combustion of reagents at 25 °C, we can very simply calculate the standard heat of any reaction at 25 °C (ΔH°_{298}) with the aid of Hess's law, as was shown in an earlier section.

Chemical reactions usually proceed in various processes in conditions differing from standard ones. It therefore becomes necessary to reduce the standard heat of a reaction to real conditions. The heat of a reaction changes comparatively slightly with a change in pressure. Hence, the influence of pressure is usually disregarded in technical calculations. For a high pressure, a correction for the pressure must be taken into account in especially accurate calculations. We consider the influence of pressure on the heat of a reaction in Chap. 5.

The temperature dependence of the heat of a reaction is expressed by the Kirchhoff equation

$$\left(\frac{\partial Q_p}{\partial T}\right)_p = \Delta C_p \tag{1.86}$$

where $\Delta C_p = \sum v''_i C''_p - \sum v'_i C'_p$, here v''_i and v'_i are the stoichiometric coefficients of the products and reactants, respectively, and C''_p and C'_p are the heat capacities of the products and reactants, respectively.

When $p = \mathrm{const}$, we have $Q_p = \Delta H$, and Eq. (1.86) can be written as follows:

$$\frac{d(\Delta H)}{dT} = \Delta C_p \quad \text{and} \quad d(\Delta H) = \Delta C_p \, dT \tag{1.87}$$

To integrate the right-hand side of this equation, we must know the functional dependence of the heat capacity on temperature, i.e. $C_p = \varphi(T)$. Such a relationship is generally given in the form of the temperature series described by Eq. (1.77).

A reaction results in a change in the heat capacity of the reagents:

$$\Delta C_p = \Delta a + \Delta b T + \Delta c T^2 + \dots \tag{1.88}$$

where Δa, Δb, Δc, ... are the differences between the sums of the corresponding coefficients in the equation $C_p = \varphi(T)$ for the products and the reactants with account taken of their stoichiometric coefficients.

Using Eq. (1.88) in (1.87) and finding the integral, we get

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta a \,(T_2 - T_1) + \frac{1}{2}\,\Delta b \,(T_2^2 - T_1^2) +$$
$$+ \frac{1}{3}\,\Delta c \,(T_2^3 - T_1^3) + \dots \tag{1.89}$$

where ΔH_{T_1} and ΔH_{T_2} are the heats of the reaction at constant pressure and the temperature T_1 and T_2, respectively.

If we assume that $T_1 = 298$ K and $p = 1$ atm, Eq. (1.89) becomes

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \Delta a \, (T - 298) + \frac{1}{2} \, \Delta b \, (T^2 - 298^2) +$$

$$+ \frac{1}{3} \, \Delta c \, (T^3 - 298^3) + \ldots \qquad (1.90)$$

where ΔH_{298}° and ΔH_T° are the standard heats of the reaction at 298 K and the required temperature T, respectively.

If we take $T_1 = 0$ K as the lower limit of integration of Eq. (1.87), then

$$\Delta H_T^\circ = \Delta H_0^\circ + \Delta a T + \frac{1}{2} \, \Delta b T^2 + \frac{1}{3} \, \Delta c T^3 + \ldots \qquad (1.91)$$

where ΔH_0° is an integration constant that can be called the *hypothetic heat of a reaction* at the temperature of absolute zero.

Equation (1.91) gives the temperature dependence of the heat of a reaction in the general form.

If we use the mean heat capacities for a given temperature interval (from T_1 to T_2) in our calculations, we can employ the equation

$$\Delta H_{T_2} = \Delta H_{T_1} + (\Delta \overline{C}_p)_{T_1 - T_2} (T_2 - T_1) \qquad (1.92)$$

It gives quite satisfactory results even for a broad temperature interval.

Thus, to calculate the heat of a reaction for any temperature, we must know: (1) the temperature dependence of the heat capacity for the reagents; and (2) the heat of the reaction for any other temperature.

The heat of a reaction can also be found graphically according to Kirchhoff's equation. For calculations by Eqs. (1.90) and (1.91), the heat of a reaction at 298 K and the coefficients a, b, c, ... of the relationship $C_p^\circ = \varphi \, (T)$ are found in tables of standard thermodynamic quantities (for example in Appendix 1). If these tables do not contain the quantities of interest to us, we use the empirical methods treated above to find them, for example the method of introducing corrections for the substitution of hydrogen by $-CH_3$ groups.

It follows from the obtained equations of $\Delta H = \psi \, (T)$ that with a change in temperature the heat of a reaction is affected by the sign of ΔC_p. When $\Delta C_p > 0$, the heat of a reaction diminishes for an exothermic reaction ($\Delta H < 0$) with increasing temperature, and it grows for an endothermic one ($\Delta H > 0$). When $\Delta C_p < 0$, the heat of an exothermic reaction grows with increasing temperature, and that of an endothermic one diminishes.

The nature of the change in the heat of a reaction ΔH with temperature depends on how ΔC_p changes with temperature. Figure 1 shows schematically all the cases of the temperature dependence of ΔC_p

and ΔH except for the one when the curves of $\sum (C_p)_r$ and $\sum (C_p)_{pr}$ are equidistant. Consequently, ΔH is a linear function of temperature. An extremum is observed comparatively seldom on the curves of $\Delta H = \psi (T)$ because the range of temperatures used is not very great. The very possibility of the appearance of an extremum, however, points to the fact that the temperature dependence of the heat of a reaction must not be extrapolated beyond the range of experimental data or the guaranteed accuracy.

Frequently approximate equations can be used to assess the heat of a reaction at any temperature T. Thus, for reactions proceeding in the gaseous phase within a comparatively narrow temperature interval and for reactions in the solid and liquid phases within a sufficiently broad temperature interval, we can consider that $\Delta C_p =$ $= $ const. Therefore, the dependence of ΔH on T will be linear

$$\Delta H_T^{\circ} = \Delta H_o^{\circ} + \Delta a T \qquad (1.93)$$

Here it is good to assume that $\Delta a = \Delta C_{p.~298}^{\circ}$ because $C_{p.~298}^{\circ}$ for the majority of the most important substances is known with a high degree of accuracy. For the case when ΔH_{298}° is very great (of the order of magnitude of tens and hundreds of thousands of calories), we can even assume that $\Delta C_p^{\circ} \approx 0,$ i.e. consider that the heat of
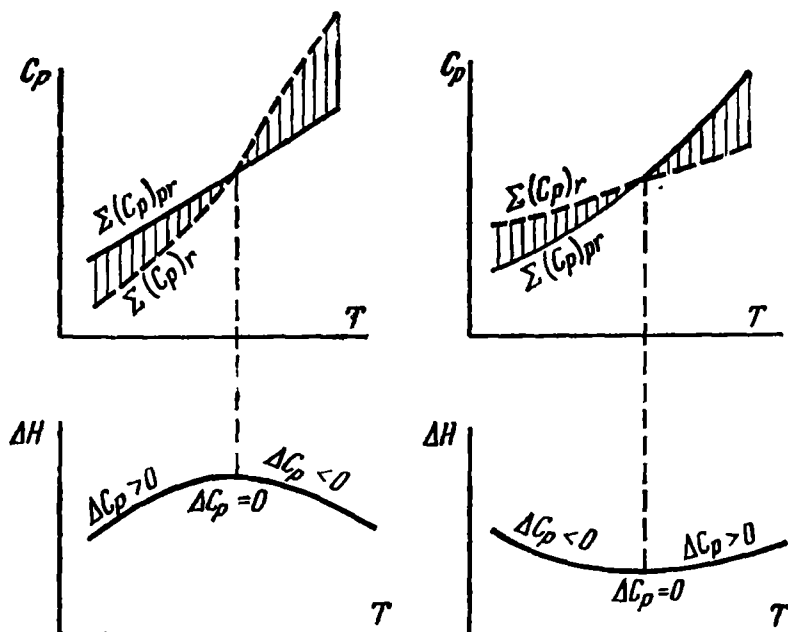
Fig. 1
Dependence of change in heat capacity ΔC_p as a result of a reaction and of ΔH of a reaction on the temperature T

a reaction does not depend on the temperature:

$$\Delta H_T^{\circ} \approx \Delta H_{298}^{\circ} = \text{const} \qquad (1.94)$$

because frequently the change in ΔH with a change in temperature does not exceed the error introduced by the equations $C_p = \varphi\,(T)$ and the value of ΔH_{298}°. The error connected with the assumption that $\Delta H^{\circ} \approx \text{const}$ may be much less than the error in extrapolation to a very high temperature in the full equation $\Delta H = \psi\,(T)$ obtained on the basis of low-temperature values of the heat capacities. We may therefore consider that the heat of combustion of organic substances (especially polyatomic) does not change relatively with the temperature.

The assumption that $\Delta H = \text{const}$ gives a comparatively small error, especially for reactions between solids, because the heat capacity of a compound may often be considered equal to the sum of the atomic heat capacities.

Example 49. Using Appendix 1, find the standard heat of the reaction of hydrogenation of benzene proceeding in the gaseous phase at 1000 K.

Solution. In Appendix 1 we find all the initial data needed to solve the problem:

$$C_6H_6(g) + 3H_2(g) = C_6H_{12}(g)$$

	$C_6H_6(g)$	$3H_2(g)$	$C_6H_{12}(g)$
$(\Delta H_{298}^{\circ})_{form}$, cal/mol	19 820	0	$-29\ 430$
a	-8.102	6.95	-16.172
$b \times 10^3$ cal/mol·K	112.780	-0.20	162.393
$c \times 10^6$	-71.306	0.48	-91.004

The standard heat of this reaction, according to Hess's law, is

$$\Delta H_{298}^{\circ} = -29\ 430 - 19\ 820 = -49\ 250 \text{ cal}$$

The differences between the sums of the corresponding coefficients in the temperature dependence of the heat capacity of the products and the reactants are:

$$\Delta a = -16.172 - (-8.102 + 3 \times 6.95) = -28.92$$

$$\Delta b \times 10^3 = 162.393 - [112.780 + 3\,(-0.20)] = 49.013$$

$$\Delta c \times 10^6 = -91.004 - (-71.306 + 3 \times 0.48) = -21.038$$

According to Eq. (1.89), the standard heat of the reaction of hydrogenation of benzene at 1000 K is

$$\Delta H_{1000}^{\circ} = -49\ 250 - 28.92\,(1000 - 298) + \frac{1}{2} \times 49.013 \times$$

$$\times 10^{-3}\,(1000^2 - 298^2) - \frac{1}{3} \times 21.038 \times$$

$$\times 10^{-6}\,(1000^3 - 298^3) = -54\ 046 \text{ cal}$$

Example 50. Using Appendix 1, find the temperature dependence of the molar heat of vaporization of liquid ethyl alcohol for the interval from 283 to 348 K at $p = 1$ atm.

Solution. The process of vaporization of a liquid can be considered as a reaction in which the reactant is the liquid and the product — the vapour. Since the temperature dependence of the heat of a reaction in the general form is described by Eq. (1.89):

$$\Delta H_T^\circ = \Delta H_0^\circ + \Delta a T + \frac{1}{2} \Delta b T^2 + \frac{1}{3} \Delta c T^3$$

for solution of the problem posed we must know the standard heats of formation and the coefficients of the temperature dependence of the heat capacity for the reagents:

$$C_2H_5OH(lq) \rightarrow C_2H_5OH(g)$$

	$C_2H_5OH(lq)$	$C_2H_5OH(g)$
$(\Delta H_{298}^\circ)_{form}$, cal/mol	$-66\ 353$	$-56\ 240$
a	25.46	4.946
$b \times 10^3$ cal/mol·K	-39.6	49.087
$c \times 10^6$	137.0	-23.855

We find the change in the above quantities as a result of vaporization of the liquid:

$$(\Delta H_{298}^\circ)_{vap} = -56\ 240 + 66\ 353 = 10\ 113 \text{ cal}$$

$$\Delta a = 4.946 - 25.46 = -20.514$$

$$\Delta b \times 10^3 = 49.087 + 39.6 = 88.687$$

$$\Delta c \times 10^6 = -23.855 - 137.0 = -160.855$$

To find the relationship $\Delta H = \psi(T)$ by Eq. (1.89), we have to know the integration constant ΔH_0°. It can be found if we know the heat of the reaction for any other temperature. In our case, we know the heat of vaporization at 298 K. Hence, from Eq. (1.90) we have

$$\Delta H_0^\circ = (\Delta H_{298}^\circ)_{vap} - \Delta a \times 298 - \frac{1}{2} \Delta b \times 298^2 - \frac{1}{3} \Delta c \times 298^3 =$$

$$= 10\ 113 + 20.514 \times 298 - \frac{1}{2} \times 88.687 \times 10^{-3} \times 298^2 +$$

$$+ \frac{1}{3} \times 160.855 \times 10^{-6} \times 298^3 = 15\ 972 \text{ cal}$$

Hence, the emperature dependence of the molar heat of vaporization of liquid ethyl alcohol within the considered interval will be

$$(\Delta H_T^\circ)_{vap} = 15\ 972 - 20.514 T + 44.343 \times 10^{-3} T^2 - 53.6 \times 10^{-6} T^3$$

Example 51. The standard heat of the reaction

$$CH_4 + CO_2 = 2CO + 2H_2$$
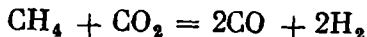
proceeding in the gaseous phase at 900 K is 260 119 J. The heat capacities of the reagents C_p° (in J/mol·K) are as follows:

	800 K	1000 K
CH_4	63.18	72.00
CO_2	40.21	42.77
CO	29.81	30.36
H_2	28.96	29.15

Find the heat ΔH_{800}° for the reaction being considered assuming that the mean heat capacity within the interval from 800 to 1000 K is

$$\Delta \overline{C}_{p,\,900}^\circ = \frac{1}{2}\,(\Delta C_{p,\,800}^\circ + \Delta C_{p,\,1000}^\circ)$$

Compare the result of the calculations with the experimental value [21] of $\Delta H_{800}^\circ = 259\,491$ J.

Solution. We find the change in the heat capacities as a result of the reaction:

$$\Delta C_{p,\,300}^\circ = 2 \times 29.81 + 2 \times 28.96 - 63.18 - 40.21 = 13.43 \text{ J/K}$$

$$\Delta C_{p,\,1000}^\circ = 2 \times 30.36 + 2 \times 29.15 - 72.00 - 42.77 = 4.25 \text{ J/K}$$

The change in the mean molar heat capacities as a result of the reaction at 900 K is

$$\Delta \overline{C}_{p,\,900}^\circ = \frac{13.43 + 4.25}{2} = 8.84 \text{ J/K}$$

If we use the mean heat capacities of the reagents, then according to Eq. (1.92)

$$\Delta H_{T_2} = \Delta H_{T_1} + [(\Delta \overline{C}_p)_{T_1-T_2}(T_2 - T_1)]$$

The required heat of the reaction is

$$\Delta H_{800}^\circ = \Delta H_{900}^\circ + [(\Delta \overline{C}_p^\circ)_{800-900}(900 - 800)] =$$
$$= 260\,119 - 8.84 \times 100 = 259\,235 \text{ J}$$

Example 52. Find graphically the heat of the reaction of dehydrogenation of ethane at 1150 K

$$2C_2H_6 = 2CH_4 + C_2H_2 + H_2$$
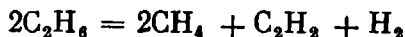
proceeding in the gaseous phase in standard conditions if the standard heat of this reaction at 298 K is 246 387 J, and the temperature dependence of the heat capacities of the reagents is expressed by the following data (in J/mol·K) [9]:

T, K . .	298	400	500	600	700	800	900	1000	1100	1200
CH_4 . .	35.73	40.73	46.57	52.51	58.07	63.18	67.82	72.00	75.69	78.99
C_2H_2 . .	43.93	50.08	54.26	57.44	60.12	62.47	64.64	66.61	68.41	70.04
H_2 . . .	28.83	29.16	29.24	29.29	29.45	29.62	29.87	30.21	30.58	30.96
C_2H_6 . .	52.63	65.60	78.07	89.33	99.24	108.07	115.85	122.71	128.74	133.97

Solution. We determine the change in the heat capacities as a result of the reaction at the given temperatures:

$$\Delta C_p = 2C_{p\,CH_4} + C_{p\,C_2H_2} + C_{p\,H_2} - 2C_{p\,C_2H_6}$$

298 K:	$\Delta C_p = 2 \times 35.73 + 43.93 + 28.83 - 2 \times 52.63 =$		38.95
400 K:	$\Delta C_p =$	$81.50 + 50.08 + 29.16 - 131.20 =$	29.54
500 K:	$\Delta C_p =$	$93.14 + 54.26 + 29.24 - 156.14 =$	20.50
600 K:	$\Delta C_p =$	$105.02 + 57.44 + 29.29 - 178.66 =$	13.09
700 K:	$\Delta C_p =$	$116.14 + 60.12 + 29.45 - 198.48 =$	7.23
800 K:	$\Delta C_p =$	$126.36 + 62.47 + 29.62 - 216.14 =$	2.00
900 K:	$\Delta C_p =$	$135.64 + 64.64 + 29.87 - 231.70 =$	-1.55
1000 K:	$\Delta C_p =$	$144.00 + 66.61 + 30.21 - 245.42 =$	-4.60
1100 K:	$\Delta C_p =$	$151.38 + 68.41 + 30.58 - 257.48 =$	-7.11
1200 K:	$\Delta C_p =$	$157.98 + 70.04 + 30.96 - 267.94 =$	-8.96

The results of our calculations are summarized below:

T, K	298	400	500	600	700	800	900	1000	1100	1200
ΔC_p°	38.95	29.54	20.50	13.09	7.23	2.00	-1.55	-4.60	-7.11	-8.96

We use the data obtained to plot a graph of the temperature dependence of ΔC_p. Next we determine the area limited by the curve $\Delta C_p = \varphi\,(T)$, perpendiculars erected from the points $T_1 = 298$ K and $T_2 = 1150$ K, and the axis of abscissas (Fig. 2).
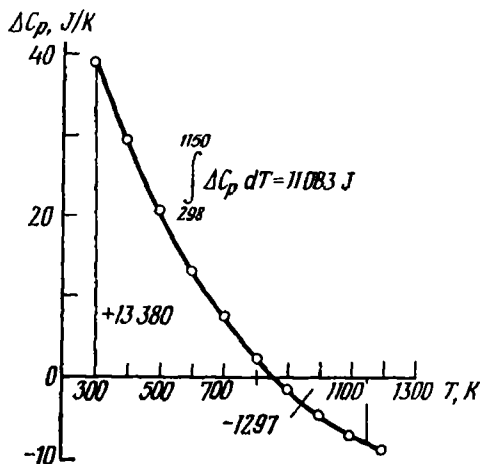
Fig. 2
Graphical determination of heat of the reaction of dehydrogenation of ethane
(Example 52)

According to the Kirchhoff equation, the heat of the reaction is

$$\Delta H^{\circ}_{1150} = \Delta H^{\circ}_{298} + \int\limits_{298}^{1150} \Delta C^{\circ}_p \, dT =$$

$$= 246\,387 + (13\,380 - 1297) = 257\,470 \ \text{J}$$

I.6
Determining the Heat of a Reaction According to the Equilibrium Constant

A reaction is written in the general form as follows:

$$\nu_1 A_1 + \nu_2 A_2 + \ldots \rightleftharpoons \nu'_1 A'_1 + \nu'_2 A'_2 + \ldots$$
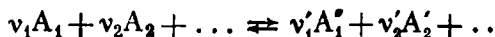
If the concentrations of the reagents are expressed through the partial pressures p_i, the equilibrium constant K_p of such a reaction will be determined according to the law of mass action from the relationship

$$K_p = \frac{p_{A'_1}^{\nu'_1} p_{A'_2}^{\nu'_2} \ldots}{p_{A_1}^{\nu_1} p_{A_2}^{\nu_2} \ldots} \tag{1.95}$$

The temperature dependence of the equilibrium constant of a reaction proceeding at constant pressure is given by the equation of a reaction isobar

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \tag{1.96}$$

where ΔH = heat of the reaction at constant pressure

R = molar gas constant (1.987 cal/mol·K, or 8.31 J/mol·K).

Equation (1.96) allows us to calculate the heat of a reaction at p = const and any temperature if we know the experimental temperature dependence of the equilibrium constant $K_p = f(T)$ for the interval from T_1 to T_2 or if we have at our disposal the numerical values of the equilibrium constants for two or more temperatures. Experience shows that the heats of reactions calculated according to thermochemical data and by Eq. (1.96) have discrepancies not exceeding 5% which is quite acceptable for many technological calculations.

Example 53. The temperature dependence of the equilibrium constant of the reaction

$$CO(g) + H_2O(g) = H_2(g) + CO_2(g)$$
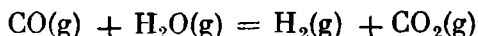
is determined by the empirical equation [9]

$$\log K_p = \frac{2116}{T} - 0.783 \log T + 0.000\,43T$$

Find the standard heat of the reaction at 25 °C using the equation of the isobar of a reaction and Hess's law. Compare the results of the calculations.

Solution. We substitute natural logarithms for common ones in the equation $K_p = f\,(T)$:

$$\ln K_p = \frac{2.303 \times 2116}{T} - 0.783 \ln T + 2.303 \times 0.000\,43T$$

We differentiate this equation with respect to temperature:

$$\frac{d \ln K_p}{dT} = -\frac{2.303 \times 2116}{T^2} - \frac{0.783}{T} + 2.303 \times 0.000\,43$$

Comparing the expression obtained with Eq. (1.96), we get

$$\frac{\Delta H}{RT^2} = -\frac{2.303 \times 2116}{T^2} - \frac{0.783}{T} + 2.303 \times 0.000\,43$$

Hence,

$$\Delta H = -2.303 \times 2116R - 0.783RT + 2.303 \times 0.000\,43RT^2$$

At $T = 298$ K

$$\Delta H^\circ_{298} = -2.303 \times 2116 \times 1.987 - 0.783 \times 1.987 \times 298 +$$
$$+ 2.303 \times 0.000\,43 \times 1.987 \times 298^2 =$$
$$= -9700 - 463 + 173 = -9900 \text{ cal}$$

We shall now determine the heat of the reaction being considered with the aid of standard heats of formation taken from tables of thermodynamic quantities (Appendix 1). The values of $(\Delta H^\circ_{298})_{\text{form}}$ for gaseous CO, H_2O, and CO_2 equal $-26\,416$, $-57\,798$, and $-94\,052$ cal/mol, respectively. Using the corollary of Hess's law. we get

$$\Delta H^\circ_{298} = -94\,052 - (-26\,416 - 57\,798) = -9838 \text{ cal}$$

Example 54. Using the temperature dependence of the equilibrium constant for the reaction

$$CO + H_2O(g) = H_2 + CO_2$$
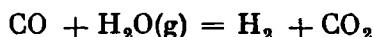
given in Example 53, determine the heat of this reaction for the temperature interval from 800 to 1000 °C, considering it to be constant and independent of the temperature.

Solution. We take a definite integral of Eq. (1.96)

$$\Delta H = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{K_2}{K_1}$$

where K_1 and K_2 are the equilibrium constants of the reaction at T_1 and T_2, respectively.

Using the empirical relationship $K_p = f(T)$ given in Example 53, we find the logarithms of the equilibrium constants at 800 and 1000 °C:

$$\log K_{p,\,1073} = 0.0093 \quad \text{and} \quad \log K_{p,\,1273} = -0.2215$$

The heat of the reaction within the interval from 1073 to 1273 K is

$$\Delta H = \frac{1.987 \times 1073 \times 1273}{1273 - 1073} \times 2.303\,(-0.2215 - 0.0093) =$$

$$= -7215 \text{ cal}$$

Example 55. The equilibrium constants of the reactions

(1) $2H_2(g) + HCOOCH_3(g) = 2CH_3OH(g)$

(2) $CH_3OH(g) + CO(g) = HCOOCH_3(g)$
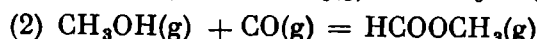
found experimentally [9] are expressed, respectively, by the equations

(3) $\log K_p^{I} = \dfrac{3149}{T} - 5.43$

(4) $\log K_p^{II} = \dfrac{1835}{T} - 6.61$

Determine the standard heat of the reaction

(5) $CO(g) + 2H_2(g) = CH_3OH(g)$
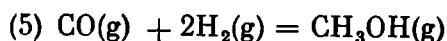
Solution. Summation of the first and second equations gives

$$\begin{array}{r} 2H_2 + HCOOCH_3 = 2CH_3OH \\ + \quad \underline{CH_3OH + CO = HCOOCH_3} \\ 2H_2 + CO = CH_3OH \end{array}$$
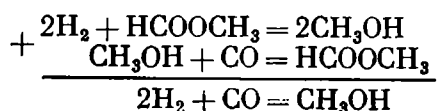
Consequently, the temperature dependence of the equilibrium constant of the fifth reaction can be obtained by summation of the third and fourth equations:

$$\log K_p^{III} = \log K_p^{I} + \log K_p^{II} = \frac{3149 + 1835}{T} - 5.43 - 6.61$$

$$\ln K_p^{III} = \frac{4984 \times 2.303}{T} - 12.04 \times 2.303$$

whence

$$\frac{d \ln K_p^{III}}{dT} = - \frac{4984 \times 2.303}{T^2}$$

$$\frac{\Delta H^\circ}{RT^2} = - \frac{4984 \times 2.303}{T^2}$$

The heat of the required reaction is

$$\Delta H^\circ = -4984 \times 2.303 \times 1.987 = -22\,800 \text{ cal}$$

Problems

1. Determine the heat of combustion of ethene in standard conditions at 25 °C:

$$C_2H_4(g) + 3O_2(g) = 2CO_2(g) + 2H_2O(lq)$$
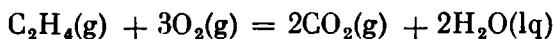
on the basis of the following data:

$$2C + 2H_2 = C_2H_4 \qquad (\Delta H^\circ_{298})_{form} = +62.01 \text{ kJ/mol}$$
$$C + O_2 = CO_2 \qquad (\Delta H^\circ_{298})_{form} = -393.9 \text{ kJ/mol}$$
$$H_2 + \frac{1}{2}O_2 = H_2O(lq) \qquad (\Delta H^\circ_{298})_{form} = -284.9 \text{ kJ/mol}$$

2. Determine the heat of the reaction

$$CH_4 + CO_2 = 2CO + 2H_2$$
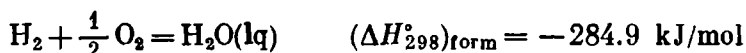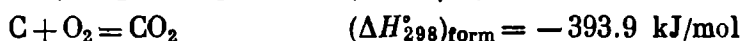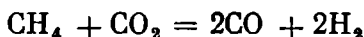
per 100 m^3 of hydrogen formed (the reaction proceeds at 0 °C and atmospheric pressure) if in the same conditions we have:

$$C + 2H_2 = CH_4 \qquad \Delta H = -75.0 \text{ kJ/mol}$$
$$C + O_2 = CO_2 \qquad \Delta H = -394.0 \text{ kJ/mol}$$
$$C + \frac{1}{2}O_2 = CO \qquad \Delta H = -110.6 \text{ kJ/mol}$$
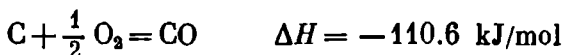
3. The values of ΔH at 200 °C and constant pressure are known for the following reactions:

$$N_2(g) + O_2(g) = N_2O(g) + \frac{1}{2}O_2(g) \qquad \qquad \Delta H = -25.3 \text{ kcal}$$

$$2N_2O(g) + 4H_2O(g) + \frac{1}{2}O_2(g) = 2NH_4NO_3(c) \quad \Delta H = -30.3 \text{ kcal}$$

Find the heat of the reaction

$$2N_2(g) + 4H_2O(g) + O_2(g) = 2NH_4NO_3(c)$$
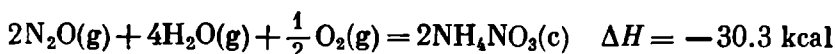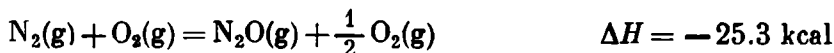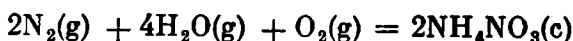
in the same conditions.

4. Using the following heats of reactions at 0 °C and constant pressure:

$$C + O_2 = CO_2 \qquad \Delta H = -97\,000 \text{ cal/mol}$$

$$CO + \frac{1}{2} O_2 = CO_2 \qquad \Delta H = -68\,000 \text{ cal/mol}$$

$$H_2 + \frac{1}{2} O_2 = H_2O(g) \qquad \Delta H = -59\,000 \text{ cal/mol}$$

find the heats of the following reactions proceeding in the same conditions:

$$C + \frac{1}{2} O_2 = CO$$

$$C + 2H_2O(g) = CO_2 + 2H_2$$

$$C + H_2O(g) = CO + H_2$$

$$2CO = CO_2 + C$$
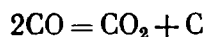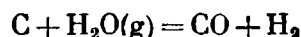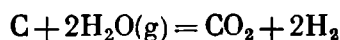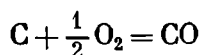
5. Find the heat of formation of SO_3 from simple substances in standard conditions at 25 °C using the following data:

$$S + O_2 = SO_2 \qquad \Delta H_{298}^\circ = -70\,200 \text{ cal/mol}$$

$$SO_2 + aq = SO_2\,aq \qquad \Delta H_{298}^\circ = -8000 \text{ cal/mol}$$

$$SO_2\,aq + Cl_2 + 2H_2O =$$

$$= H_2SO_4\,aq + 2HCl\,aq \qquad \Delta H_{298}^\circ = -73\,900 \text{ cal/mol}$$

$$H_2 + Cl_2 + aq = 2HCl\,aq \qquad \Delta H_{298}^\circ = -78\,600 \text{ cal/mol}$$

$$SO_3 + H_2O = H_2SO_4\,aq \qquad \Delta H_{298}^\circ = -18\,000 \text{ cal/mol}$$

$$H_2 + \frac{1}{2} O_2 = H_2O \qquad \Delta H_{298}^\circ = -68\,400 \text{ cal/mol}$$
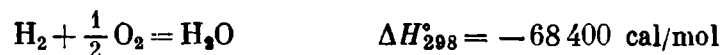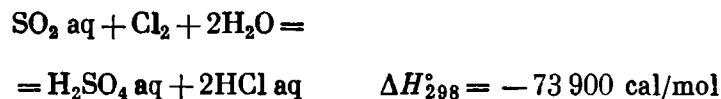
6. The heat of combustion of benzoic acid C_6H_5COOH at 17 °C at constant pressure is $\Delta H = -772\,100$ cal/mol. The heats of formation of water and carbon dioxide from simple substances in the same conditions equal $-68{,}300$ and $-94\,270$ cal/mol, respectively. Find the heat of formation of C_6H_5COOH from simple substances.

7. Find the heat of the reaction

$$CH_4 + Cl_2 = CH_3Cl + HCl$$
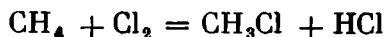
proceeding in standard conditions at 25 °C, knowing the heats of the following reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O(lq) \qquad \Delta H^\circ_{298} = -212.76 \text{ kcal}$$

$$CH_3Cl + \frac{3}{2}O_2 = CO_2 + H_2O(lq) + HCl \quad \Delta H^\circ_{298} = -164.0 \text{ kcal}$$

$$H_2 + \frac{1}{2}O_2 = H_2O(lq) \qquad \Delta H^\circ_{298} = -68.317 \text{ kcal}$$

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 = HCl \qquad \Delta H^\circ_{298} = -22.06 \text{ kcal}$$
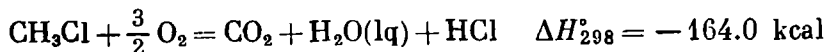
which proceed in the same conditions.

8. The heat of formation of liquid aniline $C_6H_5NH_2$ from simple substances in standard conditions at 298.15 K is 7.2 kcal/mol. Find the heat of combustion of aniline vapour in the same conditions if its heat of vaporization is 104.04 cal/g, and the heats of formation of carbon dioxide and water are —94.052 and —68.317 kcal/mol, respectively.

9. The standard heats of combustion of 2-butene and butane at 25 °C are —649.66 and —687.94 kcal/mol, respectively. Find the heat of the reactions

$$4C + 4H_2 = C_4H_8$$
$$4C + 5H_2 = C_4H_{10}$$
$$C_4H_8 + H_2 = C_4H_{10}$$
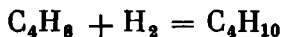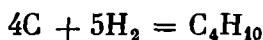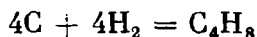
if the values of $(\Delta H^\circ_{298})_{form}$ for CO_2 and liquid water are —94.052 and —68.317 kcal/mol, respectively. Assess the accuracy of the results of these calculations if the heats of these reactions given in Appendix 1 are —0.030, —30.15, and —30.12 kcal, respectively.

10. Calculate the heat of the reaction

$$NH_3 + \frac{5}{4}O_2 = NO + \frac{3}{2}H_2O(g)$$
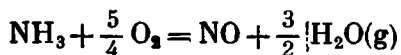
proceeding in standard conditions at 25 °C according to the following data:

$$H_2O(g) = H_2O(lq) \qquad \Delta H^\circ_{298} = -10.520 \text{ kcal/mol}$$

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3 \qquad \Delta H^\circ_{298} = -11.040 \text{ kcal/mol}$$

$$H_2 + \frac{1}{2}O_2 = H_2O(lq) \qquad \Delta H^\circ_{298} = -68.320 \text{ kcal/mol}$$

$$NO = \frac{1}{2}N_2 + \frac{1}{2}O_2 \qquad \Delta H^\circ_{298} = -21.600 \text{ kcal/mol}$$
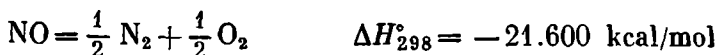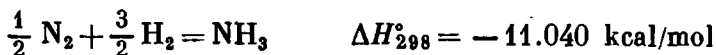
11. Using the values of $(\Delta H^{\circ}_{298})_{form}$ for ethyl alcohol, acetic acid, ethyl acetate, and water, calculate the standard heat of the reaction

$$C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$$
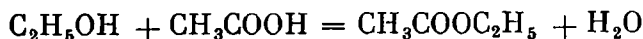
proceeding in the liquid phase at 25 °C.

12. Find the standard heat of formation of liquid *n*-heptane from simple substances if $(\Delta H^{\circ}_{298})_{comb} = -1150.77$, and the standard heats of formation of CO_2 and H_2O are -94.052 and -68.317 kcal/mol, respectively. Compare the result of the calculations with $(\Delta H^{\circ}_{298})_{form} = -53.630$ kcal/mol indicated in Appendix 1.

13. For liquid 2,2,3-trimethylbutane, we have $(\Delta H^{\circ}_{298})_{comb} = -1147.97 \pm 0.12$ kcal/mol. Using the initial conditions of Problem 12, find ΔH°_{298} for the reaction of isomerization of liquid *n*-heptane to liquid 2,2,3-trimethylbutane and compare it with the experimental value of -3.00 ± 0.22 kcal.

14. Using the standard heats of combustion at 25 °C (Appendix 1), determine $(\Delta H^{\circ}_{298})_{form}$ for the following compounds: (a) benzene C_6H_6(lq); (b) ethene glycol $C_2H_6O_2$(lq); (c) solid hydroquinone $C_6H_6O_2$; and (d) aniline $C_6H_5NH_2$(lq).

15. Knowing that at 1 atm and 298.15 K the heats of combustion of ethane, methane, and hydrogen are -1562, -891.2, and -286 kJ/mol, respectively, calculate the standard heat of the following reaction at 298.15 K:

$$C_2H_6 + H_2 = 2CH_4$$

16. Find the standard heat of the reaction

$$C + 2S = CS_2$$

at 25 °C, using the following data:

$$S + O_2 = SO_2 \qquad \Delta H^{\circ}_{298} = -297.5 \text{ kJ}$$
$$CS_2 + 3O_2 = CO_2 + 2SO_2 \qquad \Delta H^{\circ}_{298} = -1109.9 \text{ kJ}$$
$$C + O_2 = CO_2 \qquad \Delta H^{\circ}_{298} = -394 \text{ kJ}$$
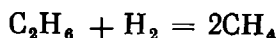
17. Calculate $(\Delta H^{\circ}_{298})_{form}$ for the compounds indicated below if their standard heats of combustion at the same temperature are known (Appendix 1): (1) formic acid CH_2O_2(lq); (2) acetaldehyde C_2H_4O(g); (3) ethene glycol $C_2H_6O_2$(lq); (4) glycerine $C_3H_8O_3$(lq); (5) 1,2-dioxane $C_4H_8O_2$(lq); (6) phenol C_6H_6O(c); (7) *o*-phthalic acid $C_8H_6O_4$(c); (8) urea (carbamide) CH_4N_2O(c); (9) methylamine CH_5N(lq); (10) methyl cyanide C_2H_3N(lq); (11) glycine (glycol) $C_2H_5NO_2$(c); (12) dimethylamine C_2H_7N(lq); (13) pyridine C_5H_5N(lq); (14) nitrobenzene $C_6H_5NO_2$(lq); and (15) aniline C_6H_7N(lq).

Take into account that the oxides $CO_2(g)$, $H_2O(lq)$, and $NO(g)$ are the combustion products. Assume:

$$C + O_2 = CO_2(g) \qquad (\Delta H^\circ_{298})_{form} = -94.052 \ \text{kcal/mol}$$

$$H_2 + \frac{1}{2} O_2 = H_2O(lq) \qquad (\Delta H^\circ_{298})_{form} = -68.370 \ \text{kcal/mol}$$

$$\frac{1}{2} N_2 + \frac{1}{2} O_2 = NO(g) \qquad (\Delta H^\circ_{298})_{form} = +21.477 \ \text{kcal/mol}$$
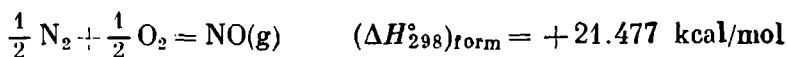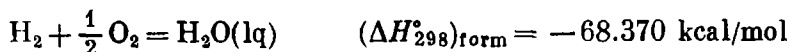
Compare the calculated values with those of $(\Delta H^\circ_{298})_{form}$ given in Appendix 1.

18. Calculate the standard heat of the reaction

$$CO(g) + NH_3(g) = HCN(g) + H_2O(g)$$
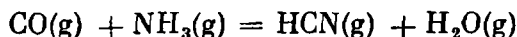
at 25 °C using the values of $(\Delta H^\circ_{298})_{form}$ for the compounds participating in the reaction.

19. The values of $(\Delta H^\circ_{298})_{form}$ for C_2H_2, CO_2, and $H_2O(lq)$ are 54 190, —94 052, and —68 317 cal/mol, respectively. How much heat is liberated upon the combustion of five moles of C_2H_2?

20. Coal containing 65 % of C is burnt in a furnace. The flue gases contain 13 % (molar) of CO_2 and 1 % of CO, the remainder being nitrogen and oxygen. Determine the heat of combustion of 1 kg of coal if it is known that the heats of formation of CO_2 and CO are —94 052 and —26 416 cal/mol, respectively.

21. Upon the combustion of hydrogen in a calorimetric bomb with the formation of liquid water, the heat of the reaction

$$2H_2 + O_2 = 2H_2O(lq)$$
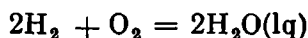
at constant volume is $\Delta U = -134\,960$ cal/mol ($V = const$). The heat of the reaction at constant pressure is $\Delta H = -136\,700$ cal/mol. Show that the experimental data agree quite adequately with those calculated by Eq. (1.21). The temperature of the experiment was 18 °C.

22. Prove that the heats of formation of hydrogen sulphide from gaseous hydrogen and solid sulphur at constant pressure and constant volume are identical at the same temperature.

23. May the difference between ΔH°_{273} and ΔU°_{273} for the reaction

$$C + CO_2 = 2CO$$
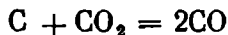
be ignored if at 0 °C and 1 atm the molar volumes of CO_2 and CO are 22 257 and 22 404 cm³, respectively, and the density of carbon is 2.255 g/cm³? The heats of oxidation of carbon and carbon monoxide to carbon dioxide in the same conditions are —94.052 ± ± 0.010 and —67.636 ± 0.029 kcal/mol, respectively.

24. The values of $(\Delta H^\circ_{298})_{form}$ for liquid water and carbon dioxide equal —68 320 and —94 050 cal/mol, respectively. The standard

heat of combustion of methane at 25 °C is —211 930 cal/mol. Determine the standard heats of formation of methane from simple substances at constant pressure and constant volume at 25 °C.

25. Calculate the heat of the following reactions at 25 °C if (a) the system is under constant pressure (ΔH); and (b) the system has constant volume (ΔU):

(1) $2H_2 + CO = CH_3OH(lq)$

(2) $4HCl + O_2 = 2H_2O(lq) + 2Cl_2$

(3) $2N_2 + 6H_2O(lq) = 4NH_3 + 3O_2$

(4) $4NO + 6H_2O(lq) = 4NH_3 + 5O_2$

(5) $2NO_2 = 2NO + O_2$

(6) $N_2O_4 = 2NO_2$

(7) $CO + 3H_2 = CH_4 + H_2O(lq)$

(8) $CO_2 + 4H_2 = CH_4 + 2H_2O(lq)$

(9) $C_2H_6 = C_2H_4 + H_2$

(10) $C_2H_5OH(lq) = C_2H_4 + H_2O$

(11) $CH_3CHO(g) + H_2 = C_2H_5OH(lq)$

(12) $C_6H_6(lq) + 3H_2 = C_6H_{12}(lq)$

Take the corresponding values of $(\Delta H^\circ_{298})_{form}$ from Appendix 1.

26. For water $(\Delta H^\circ_{298})^{lq}_{form} = -68.317$ and $(\Delta H^\circ_{298})^g_{form} = -57.798$ kcal/mol. Find the standard molar heat of vaporization of water.

27. Find the standard heat of the reaction

$$C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$$
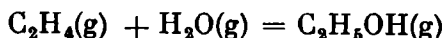
at 25 °C if at the same temperature $(\Delta H^\circ_{298})_{form}$ for ethene, water vapour, and ethanol in the vaporous state equals 12.496, —57.798, and —56.510 kcal/mol, respectively.

28. Using Konovalov's formula, calculate the standard heat of combustion of gaseous n-hexane at 25 °C if for saturated hydrocarbons $x = 0$. Compare the result of the calculations with the tabulated value of $(\Delta H^\circ_{298})_{comb} = -1002.57$ kcal/mol (Appendix 1).

29. Using Eq. (1.26), find $(\Delta H^\circ_{298})_{comb}$ for gaseous cinnamic aldehyde $C_6H_5CH{=}CHCHO$. Compare the result obtained with the published value $(\Delta H^\circ_{298})_{comb} = -1130$ kcal/mol [2].

30. Calculate $(\Delta H^\circ_{298})_{comb}$ for the following organic substances in the gaseous state. Use Konovalov's equation for the calculations. Compare the results obtained with the values of $(\Delta H^\circ_{298})_{comb}$ given in reference books [1, 2] (in kcal/mol):

(1) isobutane C_4H_{10} —686.34; (2) *n*-nonane C_9H_{20} —1474.90; (3) carbon oxysulphide COS —132.20; (4) chloromethane CH_3Cl —164.70; (5) toluene $C_6H_5CH_3$ —943.58; (6) 1-hexene C_6H_{12} —964.26; (7) acetylene C_2H_2 —310.62; and (8) ethene C_2H_4 —337.23.

31. Find $(\Delta H^\circ_{298})_{comb}$ for liquid ethyl acetate if the heat correction for the bond in aliphatic esters is —16.5 kcal. Use Eq. (1.26) for the calculations. Compare the result with the experimental value of $(\Delta H^\circ_{298})_{comb} = -538.5$ kcal/mol.

32. Calculate $(\Delta H^\circ_{298})_{comb}$ for liquid allyl alcohol $CH_2=CHCH_2OH$ and *o*-nitrotoluene $CH_3C_6H_4NO_2$. Use Kharasch's formula for the calculations. Compare the results of the calculations with $(\Delta H^\circ_{298})_{comb}$ equal to —442.6 and —899.2 kcal/mol, respectively, given in [2].

33. Using Kharasch's method, assess $(\Delta H^\circ_{298})_{comb}$ for the liquid organic substances given below. Compare the results of the calculations with the experimental values of $(\Delta H^\circ_{298})_{comb}$ given in [2] (in kcal/mol): (1) methyl alcohol CH_3OH —173.67; (2) glycerine $CH_2OH-CHOH-CH_2OH$ —397.8; (3) acetone CH_3COCH_3 —430.9; (4) diethyl ether $C_2H_5OC_2H_5$ —652.7; (5) acetic acid CH_3COOH —208.3; (6) nitrobenzene $C_6H_5NO_2$ —740.4; and (7) aniline $C_6H_5NH_2$ —811.9.

34. Using the method of increments, calculate $(\Delta H^\circ_{298})_{comb}$ for the following compounds: (a) gaseous *n*-nonane; (b) liquid *n*-nonane; and (c) gaseous 1-nonene. Compare the results with the experimental values of $(\Delta H^\circ_{298})_{comb}$ [3]: (a) —1473.40 ± 0.72; (b) —1462.91 ± ± 0.37; and (c) —1434.90 ± 0.80 kcal/mol.

35. Find $(\Delta H^\circ_{298})_{comb}$ for gaseous and liquid 3,3-diethylpentane and $(\Delta H^\circ_{298})_{form}$ for this compound in the gaseous state. Use Tatevsky's method for the calculations.

36. Using Appendix 4, determine $(\Delta H^\circ_{298})_{comb}$ for gaseous: (a) 2-methyl-3-ethylhexane; (b) 2,2,4,4-tetramethylpentane; (c) 3-ethyloctane; (d) 4-methyl-5-ethylheptane; and (e) *n*-octane.
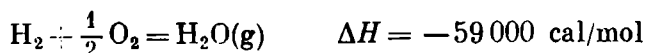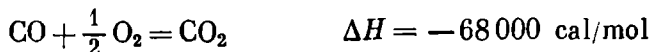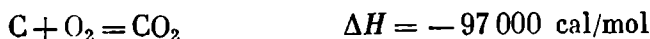
37. Using Tatevsky's method, calculate the heat of the reaction of isomerization of *n*-hexane to 2,2-dimethylbutane. The reaction proceeds in standard conditions in the gaseous phase. Perform the calculations on the basis of (a) $(\Delta H^\circ_{298})_{comb}$ and (b) $(\Delta H^\circ_{298})_{form}$ at 25 °C for the reagents. Compare the results of the calculations.

38. Assess $(\Delta H^\circ_{298})_{comb}$ for gaseous 1,3-butadiene. Use Laidler's method for the calculations. Compare the result with the experimental value of $(\Delta H^\circ_{298})_{comb} = -618.10$ kcal/mol given in [3].

39. Find $(\Delta H^\circ_{298})_{comb}$ for liquid tertiary butyl alcohol. Use Appendix 5 for the calculations. Compare the result of the calculations with $(\Delta H^\circ_{298})_{comb}$ given in Appendix 1.

40. Using Laidler's method, determine $(\Delta H^\circ_{298})_{form}$ for gaseous 2,3-dimethyl-2-butene. Compare the result with $(\Delta H^\circ_{298})_{form} = = -15.91$ kcal/mol given in [20].

41. Having first determined $(\Delta H^\circ_{298})_{comb}$ for liquid 2,2,3-trimethylbutane according to the method of Tatevsky and Laidler, find the standard molar heat of its vaporization at 25 °C. Compare the results with $(\Delta H^\circ_{298})_{vap} = 7.64$ kcal/mol given in [22].

42. Determine $(\Delta H^\circ_{298})_{form}$ for ethylene and ethane using the bond energies. Compare the results with $(\Delta H^\circ_{298})_{form}$ given in Appendix 1 (12.8 and —20.236 kcal/mol. respectively).

43. Calculate $(\Delta H^\circ_{298})_{form}$ for gaseous methyl acetate CH_3COOCH_3 and acetic acid CH_3COOH using the method of bond energies.

44. Use the bond energies to calculate the heat of the reaction

$$C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$$
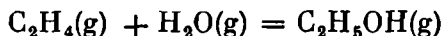
proceeding at 25 °C in standard conditions if the bond energies have the following values: $\varepsilon_{C-H} = 85.5$, $\varepsilon_{C=C} = 101.2$, $\varepsilon_{O-H} = 110$, $\varepsilon_{C-C} = 62.8$, and $\varepsilon_{C-O} = 75$ kcal/mol. Compare the result of calculating the value of ΔH°_{298} with the value calculated according to the heats of formation $(\Delta H^\circ_{298})_{form}$, which equal 12.56, —57.801, and —56.51 kcal/mol, respectively.

45. Find the standard heat of the reaction of dehydrogenation of one mole of gaseous ethyl alcohol to acetaldehyde at 25 °C. Use the bond energies for the calculations. Compare the result with the value determined according to the heats of combustion.

46. Determine the standard heat of the reaction of preparing styrene from gaseous cinnamic acid at 25 °C

$$C_6H_5CH = CHCOOH(g) \rightarrow C_6H_5CH = CH_2(g) + CO_2(g)$$
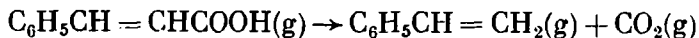
Use the bond energies to solve this problem.

47. Find $(\Delta H^\circ_{298})_{form}$ for liquid *n*-heptane if its standard molar heat of vaporization at the same temperature is 8.70 kcal/mol [20]. Calculate $(\Delta H^\circ_{298})_{form}$ for gaseous *n*-heptane by the method of increments using Eq. (1.40). Compare the result of calculating $(\Delta H^\circ_{298})^{lq}_{form}$ with the corresponding value given in [20] (—53.63 kcal/mol) and that calculated by Eq. (1.41).

48. Using the method of increments, calculate $(\Delta H^\circ_{298})_{form}$ for the following gaseous alkenes: (a) 1-nonene; (b) 1-dodecene; and (c) 1-eicosene. Compare the results of the calculations with published values [20] (in kcal/mol): (a) —24.74; (b) —39.52; and (c) —78.93.

49. Calculate $(\Delta H^\circ_{298})_{form}$ for the following gaseous substances: (a) *n*-hexylcyclopentane $C_{11}H_{22}$; (b) *n*-undecylcyclopentane $C_{16}H_{32}$; (c) *n*-hexadecylcyclopentane $C_{21}H_{42}$; (d) *n*-propylcyclohexane C_9H_{18}; (e) *n*-octylcyclohexane $C_{14}H_{28}$; and (f) *n*-pentadecylcyclohexane $C_{21}H_{44}$. Use the empirical equations (1.43) and (1.44) for the calculations. Compare the results obtained with the values given in [20]: (a) —50.07; (b) —74.70; (c) —99.33; (d) —46.20; (e) —70.65; and (f) —105.14 kcal/mol.

50. Using Eq. (1.45), find $(\Delta H^{\circ}_{298})_{\text{form}}$ for n-hexadecylbenzene $C_{22}H_{38}$ in the idealized gaseous state. Compare the result with the value -62.41 kcal/mol given in [9].

51. Using the empirical method of Anderson et al, find $(\Delta H^{\circ}_{298})_{\text{form}}$ for gaseous: (a) C_2H_5Cl; and (b) CH_2FCH_2OH. Compare the results with the values given in [20]: (a) -25.3; and (b) -96.6 kcal/mol.

52. Using Appendix 7, calculate $(\Delta H^{\circ}_{298})_{\text{form}}$ for gaseous methylacetylene and 2,3-dimethylhexane. Compare the results with the values given in [20]: 46.017, and -52.13 kcal/mol.

53. Use Appendix 7 to find $(\Delta H^{\circ}_{298})_{\text{form}}$ for gaseous chloral hydrate $CCl_3CH(OH)_2$. The tabulated value [20] is -103.6 kcal/mol.

54. Use Appendix 7 to calculate $(\Delta H^{\circ}_{298})_{\text{form}}$ for gaseous 2,2,3,3-tetramethylbutane.

55. Using the empirical method of introducing corrections for the substitution of hydrogen by $-CH_3$ and other groups, calculate $(\Delta H^{\circ}_{298})_{\text{form}}$ for the following compounds in the gaseous state: (a) benzaldehyde C_6H_5CHO; (b) acetone CH_3COCH_3; (c) chlorthoxylene $CH_3C_6H_4CH_2Cl$; and (d) stilbene $C_6H_5HC{=}CHC_6H_5$ *(trans)*.

56. The values of $(\Delta H^{\circ}_{298})_{\text{form}}$ for gaseous carbon tetrachloride, carbon tetraiodide, carbon tetrabromide, and carbon tetrafluoride, according to [20], are -25.5, 73.0, 12.0, and -212.7 kcal/mol, respectively. Using Maslovs' method, find $(\Delta H^{\circ}_{298})_{\text{form}}$ for the following completely substituted methane halides in the gaseous state: (1) CI_3Cl; (2) CBr_3F; (3) CI_3F; (4) CCl_3F; (5) CF_3Cl; (6) CBr_3Cl; (7) CF_3Br; (8) CCl_3Br; (9) CI_3Br; (10) CF_3I; (11) CCl_3I; (12) CBr_3I; (13) CBr_2F_2; (14) CI_2F_2; (15) CBr_2Cl_2; (16) CI_2Cl_2; (17) CI_2Br_2; (18) CBr_2FCl; (19) CI_2FCl; (20) CCl_2FBr; (21) CI_2FBr; (22) CCl_2FI; (23) CBr_2FI; (24) CF_2BrCl; (25) CI_2BrCl; (26) CBr_2ICl; (27) CF_2ICl; (28) CF_2BrI; (29) CCl_2BrI; and (30) CCl_2BrF. Compare the results obtained with the values of $(\Delta H^{\circ}_{298})_{\text{form}}$ given in [50]: (1) $+49$; (2) -44; (3) $+2$; (4) -72; (5) -166; (6) $+3$; (7) -156; (8) -16; (9) $+58$; (10) -141; (11) -0.8; (12) $+27$; (13) -100; (14) -70; (15) -7; (16) $+24$; (17) $+43$; (18) -54; (19) -23; (20) -63; (21) -14; (22) -48; (23) -29; (24) -110; (25) $+33$; (26) $+18$; (27) -95; (28) -85; (29) $+9$; and (30) -38 kcal/mol.

57. The values of $(\Delta H^{\circ}_{298})_{\text{form}}$ for gaseous CH_4, CCl_4, CI_4, CBr_4, CF_4, $CHCl_3$, CHI_3, $CHBr_3$, CHF_3, CH_2Cl_2, CH_2I_2, CH_2Br_2, and CH_2F_2, according to [50], are -17.889, -25.5, 73, 12, -212.7, -24, 50, 6, 169, -21, 28, -1.0, and -110 kcal/mol, respectively. Using Maslovs' method, determine $(\Delta H^{\circ}_{298})_{\text{form}}$ for the following incompletely substituted methane halides in the gaseous state: (1) CH_3F; (2) CH_3Cl; (3) CH_3Br; (4) CH_3I; (5) CH_2FCl; (6) CH_2FBr; (7) CH_2FI; (8) CH_2BrCl; (9) CH_2ICl; (10) CH_2BrI; (11) CF_2HCl; (12) CF_2HBr; (13) CF_2HI; (14) CCl_2HBr; (15) CCl_2HF; (16) CBr_2HCl; (17) CBr_2HF; (18) CBr_2HI; (19) CCl_2HI; (20) CI_2HF; (21) CI_2HCl; (22) CI_2H r; (23) $CHFClBr$; (24) $CHFClI$; (25) $CHBrClI$; (26) $CHFBrI$.

Compare the results with the corresponding values of $(\Delta H^{\circ}_{298})_{\text{form}}$ given in [50]: (1) —67; (2) —20; (3) —10; (4) +5; (5) —68; (6) —59; (7) —44; (8) —12; (9) +3; (10) +12; (11) —117; (12) —108; (13) —92; (14) —14; (15) —70; (16) —5; (17) —52; (18) +20; (19) +1; (20) —21; (21) +26; (22) +35; (23) —61; (24) —46; (25) +10; and (26) —36 kcal/mol.

58. According to [50], $(\Delta H^{\circ}_{298})_{\text{form}}$ for gaseous C_2H_4, C_2F_4, C_2Cl_4, $C_2H_2Cl_2$, $C_2H_2F_2$, C_2HF_3, and C_2HCl_3 is +12.496, —151.3, —3.6, +0.8, —69, —110.4, and —1.4 kcal/mol, respectively. Use Maslovs' method to determine $(\Delta H^{\circ}_{298})_{\text{form}}$ for the following gaseous ethylene halides: (1) $C_2Cl_2F_2$; (2) C_2H_2ClF; (3) C_2H_3Cl; (4) C_2H_3F; (5) C_2ClF_3; (6) C_2Cl_2HF; and (7) C_2F_2HCl.

59. Find ΔH_{at} — the heat of formation of gaseous toluene $C_6H_5CH_3$, o-xylene $C_6H_4(CH_3)_2$, and 1,2,3,4-tetramethylbenzene $C_6H_2(CH_3)_4$ from atoms if for the same conditions we know ΔH_{at} for benzene C_6H_6 and 1,2,3-trimethylbenzene $C_6H_3(CH_3)_3$, namely, —1050.8 and —1765.66 kcal/mol, respectively [9]. Use Maslovs' method for the calculations.

60. Using Franklin's method (Appendix 9), determine $(\Delta H^{\circ}_{298})_{\text{form}}$ for the following gaseous hydrocarbons: (1) n-hexane; (2) 2,2-dimethylbutane; (3) benzene; (4) cyclohexane; (5) n-hexene-1; (6) toluene; (7) phenol; and (8) 3-ethylbutene-1. Compare the results with the values given in [20]: (1) —39.96; (2) —44.35; (3) 19.82; (4) —29.43; (5) —9.96; (6) —11.95; (7) —22.50; and (8) —12.92 kcal/mol.

61. Using Franklin's method, find ΔH°_{298} for the cyclization of n-nonane to n-propylbenzene proceeding in the gaseous phase:

$$n\text{-}C_9H_{20} = C_9H_{12} + 4H_2$$
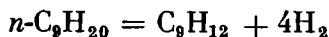
62. Determine the standard heat of alkylation of isobutane with propylene to 2,3-dimethylbutane. The reaction proceeds in the gaseous phase at 400 K. Use Appendix 9 for the calculations.

63. Using Franklin's method, find the standard heat of isomerization of ethylbenzene to orthoxylene. The reaction proceeds in the gaseous phase at 0, 298.15, and 400 K.

64. The polymerization of propylene to 1-hexene in the gaseous phase follows the equation

$$2C_3H_6 = C_6H_{12}$$
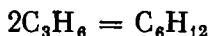
Use Franklin's method to find the standard heat of the reaction at 298.15, 400, 500, 600, 800, and 1000 K.

65. Calculate $(\Delta H^{\circ}_{298})_{\text{form}}$ for gaseous 1,1-dimethylcyclohexane C_8H_{16}. Use the method of Souders et al for the calculations. Compare the result with the value of —43.26 kcal/mol given in [20].

66. Using the group contributions of the standard heats of formation given in Appendix 10, find $(\Delta H^{\circ}_{298})_{\text{form}}$ for 2,2,3,3-tetramethyl-

butane in the idealized gaseous state. Compare the result with the value —53.99 kcal/mol given in [20].

67. Determine $(\Delta H^{\circ}_{298})_{form}$ for gaseous *trans*-pentadiene-1,3-C_5H_8. Use the empirical method of Souders et al. The published value is 18.70 kcal/mol [20].

68. Use the method of Souders et al to determine $(\Delta H^{\circ}_{298})_{form}$ for styrene (phenylethylene) in the idealized gaseous state. The published value is +35.22 kcal/mol [20].

69. Use the methods of (a) Franklin, (b) Anderson et al, and (c) Souders et al to calculate $(\Delta H^{\circ}_{298})_{form}$ for the following gaseous hydrocarbons: (1) *n*-heptane; (2) 2,2,3-trimethylbutane; (3) cyclohexane; (4) methylacetylene; (5) 1-butene; and (6) *m*-xylene. Compare the results with the following values given in [20]: (1) —44.89; (2) —48.96; (3) —29.96; (4) 44.32; (5) —0.03; and (6) 4.12 kcal/mol.

70. Using the method of Souders et al, calculate ΔH°_{400}, ΔH°_{600}, and ΔH°_{1000} for the following hydrocarbons in the idealized gaseous state: (1) propane; (2) *n*-heptane; (3) 3-methylhexane; (4) 2,4-dimethylpentane; (5) 2,2,4-trimethylbutane; (6) cyclopentane; (7) cyclohexane; (8) methylcyclopentane; (9) ethylene; (10) 1-butene; (11) 2-butene (*cis*); (12) 2-butene (*trans*); (13) 1,3-butadiene; and (14) acetylene. Compare the results with the corresponding values given in [9]: (1) —26.58, —28.86, —31.03; (2) —47.49, —51.37, —54.73; (3) —48.74, —52.73, —56.10; (4) —51.16, —55.18, —58.54; (5) —51.25, —54.88, —57.72; (6) —20.73, —24.04, —26.78; (7) —32.07, —35.53, —37.70; (8) —29.00, —32.63, —35.44; (9) 10.88, 9.77, 8.34; (10) —1.39, —3.58, —5.75; (11) —3.18, —5.69, —8.28; (12) —4.34, —6.85, —9.44; (13) 25.90, 24.65, 23.32; (14) 54.13, 54.17, 54.02 kcal/mol.

71. The experimental values of the standard heats of formation of gaseous *n*-heptane, ethylene, and acetylene (in kcal/mol) from simple substances at 400, 600, and 1000 K given in [46] are as follows:

Hydrocarbon	$(\Delta H^{\circ}_{400})_{form}$	$(\Delta H^{\circ}_{600})_{form}$	$(\Delta H^{\circ}_{1000})_{form}$
1. *n*-Heptane	—47.71	—51.82	—55.29
2. Ethylene	11.77	10.60	9.21
3. Acetylene	54.13	53.93	53.30

Using the methods of Franklin and of Souders et al, calculate $(\Delta H^{\circ}_{400})_{form}$, $(\Delta H^{\circ}_{600})_{form}$, and $(\Delta H^{\circ}_{1000})_{form}$ for these hydrocarbons. Find the discrepancies between the calculated and experimental values $(\Delta H^{\circ}_T)_{calc} - (\Delta H^{\circ}_T)_{exp}$.

72. Determine the heat needed for heating 5 g of nitrogen from 15 to 35 °C if the volume of the gas does not change, and $C_V = 5R/2$.

73. Determine the heat absorbed in heating 100 g of carbon dioxide from 15 to 1000 °C at constant volume if $C_V = 6.5 + 0.001\ 93t$ cal/mol·K.

74. The mean molar heat capacity of oxygen at constant pressure for the interval from 0 to 1500 °C is expressed by the equation

$$\overline{C}_p = (7.06 + 0.000\ 813t) \times 4.19 \text{ kJ/kmol·K}$$

Determine the mean molar, specific, and volume heat capacities at constant pressure for the interval from 0 to 1000 °C.

75. The gas obtained in underground gasification has approximately the following composition (per cent by volume): $CO-12$, H_2-14, $N_2-62.2$, CO_2-10, $CH_4-1.8$. Find the mean volume heat capacity of the gas at 0 °C if $\overline{C}_V$ for the components (in kJ/m³·K) equals 1.270, 1.295, 1.265, 1.688, and 1.487, respectively.

76. Determine the mean molar heat capacity of ammonia within the interval from 250 to 350 K if the true heat capacity is expressed by the equation

$$C_p = 5.92 + 89.63 \times 10^{-4}T - 17.64 \times 10^{-7}T^2 \text{ cal/mol·K}$$

77. Determine the number of moles and the mean heat capacity of argon if an amount of heat equal to 23.88 kcal is used to heat it from 244 to 500 °C; the initial and final volumes are 5 and 50 litres, respectively.

78. Find the mean molar heat capacity of gaseous chlorine at constant pressure within the interval from 300 to 400 K if the expression for its true heat capacity at constant volume has the form

$$C_V = 23.304 + 10.142 \times 10^{-3}T - 4.041 \times 10^{-6}T^2 \text{ J/mol·K}$$

79. The true molar heat capacity of gaseous C_2H_5OH at $p = \text{const}$ within the interval from 298 to 1500 K is given by the expression

$$C_p = 106.524 - 0.1656T + 0.5753 \times 10^{-3}T^2 \text{ J/mol·K}$$

Find the mean molar heat capacity for the interval from 0 to 78 °C.

80. The quantity $\overline{C}_V$ for carbon dioxide within the interval from 298 to 2500 K is given by the expression

$$\overline{C}_V = 21.363 + 13.97 \times 10^{-3}T + 3.075 \times 10^{-6}T^2 \text{ J/mol·K}$$

Find the true molar heat capacity at constant pressure and 0 °C.

81. The mean molar heat capacity of hydrogen at constant volume and 1700 K is 22.72, and at 2500 K is 23.848 J/mol·K. Find the mean molar heat capacity at constant pressure and 1200 K, and also

the temperature dependence of the true heat capacity at $p = \text{const}$ if the heat capacity of hydrogen changes linearly with the temperature according to the equation $\bar{C}_V = a - bT$.

82. The true molar heat capacity of butanol vapour at constant pressure depending on the temperature has the following values:

T, K	300	400	500	600	700	800	900	1000	1100
C_p, cal mol·K	2.083	2.851	3.496	4.03	4.43	4.75	4.98	5.14	5.27

Using the method of least squares, express the temperature dependence of the heat capacity by an equation of the form $C_p = a + bT + cT^2$.

83. Derive an equation for the temperature dependence of the true molar heat capacity of methane at constant pressure using the following experimental data:

T, K	300	400	500	600	700	800	900	1000
C_p°, cal/mol·K . .	8.536	9.736	11.133	12.546	13.88	15.10	16.24	17.210

Use the method of least squares.

84. Using the characteristic temperatures and Einstein's function for calculating the vibrational component (Appendices 11 and 12), calculate the true molar heat capacities at $p = 1$ atm and 298.15 K for carbon monoxide, carbon dioxide, hydrogen, oxygen, nitrogen, carbon tetrachloride, water, hydrogen sulphide, ammonia, and sulphur dioxide. Compare the results with Appendix 1.

85. Find C_p° for acetylene at 298.15, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, and 1500 K. Use Eq. (1.81) of the Planck-Einstein quantum theory of heat capacity.

86. Find the true molar standard heat capacity $C_{p,\,298}^\circ$ for gaseous $CFCl_3$ according to its known values for CF_4 and CCl_4 which, according to A. Vvedensky [25], equal 14.61 and 19.92 cal/mol·K, respectively. Use Maslovs' method. Compare the result with the experimental value of 18.61 cal/mol·K.

87. Yu. and P. Maslov propose the following expressions for calculating the true molar heat capacities at $p = \text{const}$ for methane halides [49]:

(a) $C_p^\circ{}_{CX_2YZ} = 0.5\,(C_p^\circ{}_{CX_2Y_2} + C_p^\circ{}_{CX_2Z_2})$

(b) $C_p^\circ{}_{CXYZP} = \dfrac{1}{3}\,(C_p^\circ{}_{CXY_3} + C_p^\circ{}_{CXZ_3} + C_p^\circ{}_{CXP_3})$

(c) $C_p^\circ{}_{CX_3Y} = 0.5\,(C_p^\circ{}_{CX_4} + C_p^\circ{}_{CX_2Y_2})$

(d) $C_p^\circ{}_{CX_2Y_2} = 0.5\,(C_p^\circ{}_{CX_4} + C_p^\circ{}_{CY_4})$

where X, Y, Z, and P are hydrogen or a halogen.

Determine the standard molar heat capacities at $p = \text{const}$ and 25 °C for (1) CH_2ClBr; (2) $CHClBrF$; (3) CH_3Cl; and (4) CH_2F_2 if the

following values of $C_{p,\,298}^{\circ}$ (in cal/mol·K) are known [20]: CH_2Cl_2 (12.226), CH_2Br_2 (13.09), $CHCl_3$ (15.73), $CHBr_3$ (11.61), CHF_3 (8.10), CH_4 (8.518), and CF_4 (19.866).

88. The experimental values of C_p° for gaseous *n*-hexane at different temperatures are as follows [48] (in cal/mol·K): 40.22 at 365 K, 43.30 at 399 K, 46.39 at 434 K, and 49.46 at 469 K. Assess how accurately Maslovs' Eq. (1.54) describes the above experimental data.

89. The true standard molar heat capacities at 25 °C ($C_{p,\,298}^{\circ}$) for ethene, *n*-pentene, *n*-octene, *n*-undecene, and *n*-pentadecene in the idealized gaseous state are 10.41, 27.39, 44.60, 61.88, and 84.92 cal/mol·K, respectively [48]. Using Maslovs' method, find $C_{p,\,298}^{\circ}$ for the above substances. Determine the absolute deviation between the calculated values and the values according to [48].

90. Using Maslovs' method, calculate C_p° at 25 °C for *n*-decanol-1 $C_{10}H_{22}O$ in the idealized gaseous state. Compare the result with the tabulated value of $C_{p,\,298}^{\circ} = 59.11$ cal/mol·K [20].

91. Using Maslovs' method, find the temperature dependence of C_p° in the form of the equation

$$C_p^{\circ} = a + bT + cT^2$$

for the following compounds in the idealized gaseous state: (1) *n*-butylbenzene $C_{10}H_{14}$; (2) *n*-de.ine-1 $C_{10}H_{18}$; (3) *n*-decene-1 $C_{10}H_{20}$; (4) *n*-decane $C_{10}H_{22}$; and (5) *n*-butylcyclohexane $C_{10}H_{20}$.

92. Find the temperature dependence of the true standard molar heat capacity in the form of equations of the kind

$$C_p^{\circ} = a + bT + cT^2$$

for the following organic compounds in the idealized gaseous state: (1) *n*-butyraldehyde C_4H_8O; (2) methyl butyrate $C_5H_{10}O_2$; (3) valerianic acid $C_5H_{10}O_2$; (4) *n*-amyl mercaptan $C_5H_{12}S$; and (5) methylbutyl sulphide $C_5H_{12}S$. Use Maslovs' method in the calculations.

93. Using Appendix 7, find the coefficients of the equation

$$C_p^{\circ} = a + bT + cT^2$$

for gaseous 2,2,4-trimethylpentane. Calculate the heat capacity of this substance at 442 K. Compare the result with the experimental value of $C_p^{\circ} = 64.2$ cal/mol·K [19].

94. Using the method of Anderson et al, find: (1) the temperature dependence of the true molar heat capacity at constant pressure ($p = 1$ atm) for acetone vapour $C_p^{\circ} = \varphi(T)$; (2) the values of C_p° at $T_1 = 376$ and $T_2 = 454$ K (the experimental values are 21.7 and 23.9 cal/mol·K, respectively [19]; and (3) the amount of heat needed to heat one mole of acetone vapour from 298.15 to 500 K.

95. Using the empirical method of introducing corrections for the substitution of hydrogen by $-CH_3$ and other groups, find the tem-

perature dependence of the true molar heat capacity of gaseous cumene at $p = const$ $C_p^{\circ} = \varphi(T)$ and determine C_p° at 1000 K.

96. The value of $(\Delta H_{298}^{\circ})_{form}$ for ethylene is 12.496 kcal/mol. Calculate the standard heat of formation of ethylene at 500 °C.

97. The heats of the reactions

$$C(c) + CO_2(g) = 2CO(g)$$

and

$$C(c) + H_2O(g) = CO(g) + H_2(g)$$
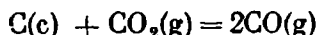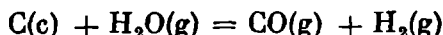
at 500 °C and at $p = const$ are 41.501 and 31.981 kcal, respe tively. Find the heat of the reaction

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$
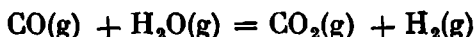
proceeding at the same pressure, but at 1000 °C if the following temperature dependences of the true molar heat capacities at $p = const$ hold for the reagents (in cal/mol·K):

$$C_{p\,CO} = 6.60 + 1.20 \times 10^{-3}T$$

$$C_{p\,H_2O} = 8.22 + 0.15 \times 10^{-3}T + 1.34 \times 10^{-6}T^2$$

$$C_{p\,CO_2} = 6.25 + 2.09 \times 10^{-3}T - 0.459 \times 10^{-6}T^2$$

$$C_{p\,H_2} = 6.62 + 0.81 \times 10^{-3}T$$

98. The molar heat of vaporization of benzene at 0 °C is 7810 cal/mol. The mean specific heat capacity of benzene vapour within the interval from 0 to 80 °C is 0.299 cal/g·K. The mean specific heat capacity of liquid benzene within the same temperature interval is 0.411 cal/g·K. Determine the molar heat of vaporization of benzene at 80 °C.

99. The mean specific heat capacity of benzene vapour within the interval from 0 to 80 °C is 0.411 cal/g·K. The mean molar heat capacity of acetylene vapour within the same temperature interval is 10.43 cal/mol·K. The heat of the reaction

$$3C_2H_2(g) = C_6H_6(g)$$
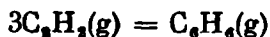
at 25 °C and constant pressure is −150 850 cal. Find the heat of this reaction at 75 °C and constant pressure.

100. Find the temperature dependence of the heat of the reaction

$$N_2 + O_2 = 2NO$$

if $\Delta H_{298}^{\circ} = 43\,200$ cal and the true molar heat capacities at $p = const$ within the temperature interval from 298 to 2500 K are giv-

en by the equations

$$C_{p\,NO}^{\circ} = 7.07 + 0.92 \times 10^{-3}T - 0.14 \times 10^{5}T^{-2}$$
$$C_{p\,N_2}^{\circ} = 6.66 + 1.02 \times 10^{-3}T$$
$$C_{p\,O_2}^{\circ} = 7.52 + 0.81 \times 10^{-3}T - 0.90 \times 10^{5}T^{-2}$$

These equations give the heat capacity in cal/mol·K.

101. Using the result obtained in solving the preceding problem, find ΔC_p° for the reaction

$$N_2 + O_2 = 2NO$$
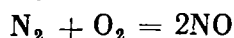
at 2000 K.

102. Find the standard heat of the reaction

$$3H_2 + N_2 = 2NH_3$$
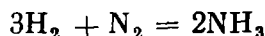
at 600 °C, constant pressure, and constant volume.

103. For the reaction

$$CaO + CO_2 = CaCO_3$$

within the temperature interval from 298 to 1200 K, we have

$$\Delta H_T = -44\,288 - 2.76T - 1 \times 10^{-3}T^2 - 2.6 \times 10^{5}T^{-1}$$

The true molar heat capacities of CaO and CO_2 within the same temperature interval at $p = $ const are

$$C_{p\,CaO} = 11.67 + 1.08 \times 10^{-3}T - 1.56 \times 10^{5}T^{-2}$$
$$C_{p\,CO_2} = 10.55 + 2.16 \times 10^{-3}T - 2.04 \times 10^{5}T^{-2}$$

Derive an equation of the dependence of C_p on T for $CaCO_3$.

104. Find the standard heat of the reaction

$$C + 2H_2 = CH_4$$

at 1000 K if its heat $\Delta H_{298}^{\circ} = -17\,903$ cal/mol and the heat capacities of the reagents are as follows (in cal/mol·K):

T, K ...	300	400	500	600	700	800	1000	1200
$C_{p\,H_2}^{\circ}$ ...	6.89	6.97	6.99	7.01	7.03	7.08	7.22	7.31
$C_{p\,C}^{\circ}$ ...	2.08	2.85	3.50	4.03	4.43	4.75	5.14	5.42
$C_{p\,CH_4}^{\circ}$ ..	8.65	9.74	11.13	12.55	13.88	15.10	17.21	18.88

105. In the polymerization of ethylene, *n*-butene is formed. The standard heats of formation of ethylene and butene (in cal/mol) are:

T, K	400	500	600	700	800	900	1000
$(\Delta H_{form}^{\circ})_{C_2H_4}$	11 760	11 138	10 600	10 142	9760	9448	9205
$(\Delta H_{form}^{\circ})_{C_4H_8}$	−1090	−2215	−3183	−3830	−4460	−4890	−5170

Find the heat capacity of *n*-butene at 800 K if at this temperature $C_{p\ C_2H_4}^{\circ} = 20.20$ cal/mol·K. Compare the result of the calculations with the value of $C_{p,\ 800}^{\circ} = 42.33$ cal/mol·K for *n*-butene found in [19].

106. For the 18 reactions listed below:

(1) find the equation expressing the temperature dependence of the standard heat of the reactions if ΔH_{298}°, the heat of the reaction at 25 °C, is known [take the equations of the relationship $C_p^{\circ} = \varphi\ (T)$ from Appendix 1];

(2) calculate the heat of the reactions at T_1;

(3) plot graphs of the temperature dependences of $\sum \nu_i\ (C_p^{\circ})_r$, $\sum \nu_i'\ (C_p^{\circ})_{pr}$ and ΔH° for the interval from 298 to T_1 K;

(4) determine graphically the value of $(\partial \Delta H / \partial T)_p$ at T_2.

		T_1, K	T_2, K
(1)	$2H_2 + CO = CH_3OH(g)$	350	390
(2)	$4HCl + O_2 = 2H_2O(g) + 2Cl_2$	650	750
(3)	$4NO + 6H_2O(g) = 4NH_3 + 5O_2$	900	1000
(4)	$2NO_2 = 2NO + O_2$	500	700
(5)	$N_2O_4 = 2NO_2$	350	400
(6)	$2SO_2 + O_2 = 2SO_3(g)$	600	700
(7)	$SO_2 + Cl_2 = SO_2Cl_2$	300	400
(8)	$CO + 3H_2 = CH_4 + H_2O(g)$	900	1000
(9)	$2CO + SO_2 = S(g) + 2CO_2$	700	900
(10)	$CO + Cl_2 = COCl_2(g)$	350	400
(11)	$CO_2 + H_2 = CO + H_2O(g)$	1000	1200
(12)	$CO_2 + 4H_2 = CH_4 + 2H_2O(g)$	900	1000
(13)	$2CO_2 = 2CO + O_2$	500	700
(14)	$CH_4 + CO_2 = 2CO + 2H_2$	320	350
(15)	$C_2H_6 = C_2H_4 + H_2$	350	400
(16)	$C_2H_5OH(g) = C_2H_4 + H_2O(g)$	300	400
(17)	$CH_3CHO(g) + H_2 = C_2H_5OH(g)$	450	500
(18)	$C_6H_6(g) + 3H_2 = C_6H_{12}(g)$	500	600

107. The temperature dependence of the molar heat capacity at constant pressure (in cal/mol·K) for methane, water vapour, carbon monoxide, and hydrogen is as follows:

T, K	900	1100	1300	1500
$C_{p\ CH_4}$	16.21	18.09	19.57	20.71
$C_{p\ H_2O}$	9.559	10.172	10.479	11.263
$C_{p\ CO}$	7.787	8.058	8.265	8.419
$C_{p\ H_2}$	7.139	7.308	7.505	7.713

Find the temperature at which $\Delta C_p = 0$ for the reaction of conversion of methane with water vapour (steam) to carbon monoxide and hydrogen.

108. A. Vvedensky proposed the following empirical equations of the temperature dependence of C_p for ethane, ethylene, and hydrogen on the basis of experimental data for the interval from 298 to 1500 K:

$$C_{p\,C_2H_6} = 1.62 + 42.1 \times 10^{-3}T - 139.0 \times 10^{-7}T^2$$

$$C_{p\,C_2H_4} = 2.08 + 31.1 \times 10^{-3}T - 106.6 \times 10^{-7}T^2$$

$$C_{p\,H_2} = 6.956 + 0.97 \times 10^{-3}T$$

Will the heat of the reaction of hydrogenation of ethylene increase or diminish with increasing temperature within the interval from 300 to 1000 K? What is the rate of its change with the temperature?

109. Use the equations

$$C_{p\,C} = 1.1 + 4.8 \times 10^{-3}T - 1.2 \times 10^{-6}T^2$$

$$C_{p\,CO} = 6.60 + 1.20 \times 10^{-3}T$$

$$C_{p\,O_2} = 6.26 + 2.746 \times 10^{-3}T - 0.770 \times 10^{-6}T^2$$

to find the temperature at which $\Delta C_p = 0$ for the reaction

$$C + \frac{1}{2}O_2 = CO$$
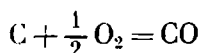
110. Compile an equation of the temperature dependence of $\Delta H°$ for the reaction of alkylation of benzene with propylene proceeding in the gaseous phase. Use (a) Appendix 1; and (b) the method of introducing corrections (Appendix 7) for the substitution of hydrogen by $-CH_3$ and other groups.

111. The temperature dependence of the equilibrium constant for the reaction of synthesis of methane from water gas

$$CO + 2H_2 = CH_3OH(g)$$
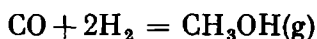
is expressed by the equation

$$\ln K_p = -\frac{17\,660}{T} - 8.82 \ln T + 0.006\,85T + 28.8$$

Find the temperature dependence of the heat of this reaction at $p = \text{const}$ using the equation of the isobar of the reaction.

112. The equilibrium constant for the reaction

$$2CH_3OH(g) = 2H_2 + HCOOCH_3(g)$$
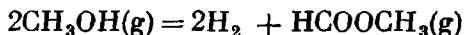
can be found from the equation $\log K_p = 3149/T - 5.43$. Determine the heat of this reaction at 400 K.

113. Determine the heat of the reaction

$$2CO + O_2 = 2CO_2$$
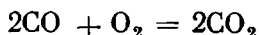
at constant pressure, considering it to be constant within the interval from 2000 to 2500 K if $K_p = 3.97 \times 10^{-1}$ at 2000 K and $K_p = 2.29 \times 10^{-5}$ at 2500 K.

114. The equilibrium constant K_p for the reaction

$$C + 2H_2 = CH_4$$
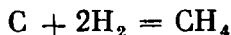
proceeding in standard conditions at 700 and 750 °C is 0.195 and 0.1175, respectively. Find the heat of this reaction for the given temperature interval and compare it with the most accurate value of $\Delta H^\circ_{1000} = -21\,430$ cal.

115. Find approximately the heat of the reaction

$$CO + H_2O(g) = CO_2 + H_2$$
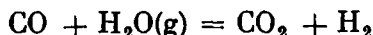
at $p = $ const if K_p at 1100 K decreases by about 0.32 % per kelvin. Assess the accuracy of the calculations if at 1100 K the heats of formation of CO, H_2O (vapour), and CO_2 are $-26\,909$, $-59\,384$, and $-94\,634$ cal/mol, respectively.

116. The temperature dependence of the equilibrium constant for the reaction

$$C_6H_6(g) + 3H_2 = C_6H_{12}(g)$$

proceeding in standard conditions within the temperature interval from 223 to 276 °C is given by the equation

$$\log K_p = \frac{9590}{T} - 9.9194 \log T + 0.002\,285T + 8.565$$

Draw up an equation for the temperature dependence of ΔH. Calculate ΔH°_{298}.

2
Entropy

All natural processes connected with a change in their energy state obey the first law of thermodynamics, but not every process that does not contradict the first law can be carried out in practice. It only follows from the first law of thermodynamics that the energy of an isolated system is constant, but this law cannot be used to determine the direction of the processes occurring in a system. Consequently, the first law is not sufficient for a complete description of thermodynamic processes. It allows us to accurately find the energy balance of processes, but gives no indications of their direction or the possibility of conducting them. We know, however, that real processes follow a definite direction, and, as a rule, we cannot make a process go on in the reverse direction without changing its conditions.

It is convenient to classify all processes as positive and negative. *Positive (spontaneous) processes* occur by themselves, for example, the expansion of a gas, diffusion, and the transfer of work into heat. *Negative (non-spontaneous) processes* do not proceed by themselves, i.e. without any external action, for example the transition of a gas from a greater to a smaller volume, and the transfer of heat into work. Only spontaneous (positive) processes occur in an isolated system where all external action is excluded.

Processes are also divided into reversible and irreversible ones. *Reversible (quasistatic) processes* when conducted in the reverse direction repeat all the stages of the direct process. *Irreversible processes* when conducted in the reverse direction do not repeat the direct process. If processes cannot become reversible in any conditions, they are called *internally irreversible*. An example is the liberation of heat due to friction. If a process in definite conditions can become reversible, it is called *conditionally irreversible*. An example is the compression and expansion of a gas.

The second law of thermodynamics makes it possible to predict the direction and establish the probability (the possibility or impossibility) of thermodynamic processes. The second law, like the first

one, is the result of summarizing human experience gained during many centuries, and, therefore, is based on an enormous amount of accumulated experimental material.

In the same way as the first law uses a function of state—the internal energy U, the second law in its form proposed by R. Clausius operates with a new function of state—entropy S. We can approach the concept of entropy by proving the theorem that any closed reversible cycle can be divided into an infinitely great number of infinitely small Carnot cycles. This theorem was proved by Clausius, and the result was an analytic expression of the second law of thermodynamics for reversible processes:

$$dS = \frac{\delta Q}{T} \tag{2.1}$$

where δQ = elementary amount of heat absorbed in a reversible process

T = temperature, K

S = thermodynamic function called entropy.

Entropy is first of all an unambiguous, continuous, and finite function of state of a system. Therefore, the change in this function in a reversible process does not depend on the path followed by a system in passing over from one state to another, but depends only on the entropy of the initial and final states of the system. Like any extensive property of a system, the entropy is proportional to the mass. Hence, it follows that the value of the entropy can be related to various amounts of a substance. It is most frequently related to one mole.

Entropy is measured in the same units as heat capacity, i.e. in cal/mol·K, cal/g·K, J/mol·K, and J/g·K. The unit 1 cal/mol·K is often called an *entropy unit* and is designated by the symbol e.u.

If in an isolated system a process being considered is attended by an increase in entropy $(+\Delta S)$, it is spontaneous, and by a decrease $(-\Delta S)$, it is non-spontaneous. In an isolated system, processes obviously stop when the entropy of the system reaches the maximum value possible for the system with some of its parameters constant, namely, with constant internal energy U and volume V (the conditions for an isolated state of the system). A further change in the state of the system would have had to cause diminishing of the entropy, which is impossible in an isolated system. Consequently, a feature of the equilibrium of a system is the maximum entropy at constant internal energy and volume.

We must bear in mind that in a non-isolated system exchanging heat and work with its surroundings, processes attended by either an increase or a decrease in the entropy of the system are possible. Hence, to unambiguously solve the problem of the direction of

a process, all the bodies participating in it should be included in the system and the latter thus made isolated.

Entropy is a very convenient function with whose aid (as will be shown below) it is quite simple to calculate the equilibria of chemical reactions.

2.1
Calculation of Entropy

The change in entropy as a result of the transition of a system from one state to another does not depend on the conditions in which the relevant process is conducted.

Let us consider the calculation of the change in entropy in some processes. If we choose V, T and p, T as the variables determining the state of a system, the analytic expressions of the first law of thermodynamics will be

$$\delta Q = l\, dV + C_V\, dT \tag{2.2}$$

$$\delta Q = h\, dp + C_p\, dT \tag{2.3}$$

where l, h, C_V, and C_p are caloric coefficients.

Introducing the integrating factor $1/T$ into Eqs. (2.2) and (2.3) and comparing the expressions obtained with the analytic expression of the second law of thermodynamics for reversible processes [Eq. (2.1)], we get

$$dS = \frac{\delta Q}{T} = \frac{l}{T}\, dV + \frac{C_V}{T}\, dT \tag{2.4}$$

$$dS = \frac{\delta Q}{T} = \frac{h}{T}\, dp + \frac{C_p}{T}\, dT \tag{2.5}$$

Using the caloric coefficients for one mole of an ideal gas in Eqs. (2.4) and (2.5):

$$l = p = \frac{RT}{V} \quad \text{and} \quad h = -V = -\frac{RT}{p} \tag{2.6}$$

and assuming that the true molar heat capacities at constant volume and pressure C_V and C_p do not depend on the temperature within a small interval of it, we get after integration

$$\Delta S = S_2 - S_1 = R \ln \frac{V_2}{V_1} + C_V \ln \frac{T_2}{T_1} \tag{2.7}$$

$$\Delta S = S_2 - S_1 = -R \ln \frac{p_2}{p_1} + C_p \ln \frac{T_2}{T_1} \tag{2.8}$$

Equations (2.7) and (2.8) permit us to calculate the change in entropy as a result of the expansion or compression of one mole of an

ideal gas. Assume that $T_1 = T_2$. Hence, from Eq. (2.7) it follows that

$$\Delta S = S_2 - S_1 = R \ln \frac{V_2}{V_1} \tag{2.9}$$

Assume that $V_2 > V_1$. Therefore, $\ln \frac{V_2}{V_1} > 0$. In this case $(S_2 - S_1) > 0$, and $S_2 > S_1$. Consequently, if a gas passes from a smaller volume to a larger one (a spontaneous process), the entropy of the system grows.

Let us analyse Eq. (2.8). If $T_1 = T_2$, then

$$\Delta S = S_2 - S_1 = R \ln \frac{p_1}{p_2} \tag{2.10}$$

If we also have $p_1 > p_2$, then $(S_2 - S_1) > 0$, and $S_2 > S_1$. And this means that when a gas passes from a greater pressure to a smaller one (a positive or spontaneous process), the entropy grows in the system.

The above examples confirm the postulate that the sign of the change in the entropy of a system can be used to determine the direction of a process.

When the pressure and volume are independent variables, by using in Eq. (2.7) or (2.8) the values of the temperatures from the equation of state of one mole of an ideal gas ($T_1 = p_1V_1/R$ and $T_2 = p_2V_2/R$), and also bearing in mind that $C_p - C_V = R$ and $C_p/C_V = \gamma$, we get

$$\Delta S = C_V \ln \frac{p_2 V_2^\gamma}{p_1 V_1^\gamma} \tag{2.11}$$

When $n_1, n_2, \ldots, n_i$ moles of different gases are mixed at constant temperature and total pressure p, then each gas changes its volume from the initial $V_1, V_2, \ldots, V_i$ to the volume of the mixture equal to the sum of the initial volumes: $V = V_1 + V_2 + \ldots + V_i$. The change in the entropy in mixing is the sum of the changes in the entropy of each gas upon its isothermal expansion. Hence, in accordance with Eq. (2.7):

$$\Delta S = R \left(n_1 \ln \frac{V}{V_1} + n_2 \ln \frac{V}{V_2} + \ldots \right) \tag{2.12}$$

And because $V > V_i$, then $\Delta S > 0$, i.e. the entropy after mixing is greater than before it.

The change in entropy as a result of heating a system from T_1 to T_2 at constant volume or constant pressure can be calculated as follows. When $V = \text{const}$, Eq. (2.4) can be written as follows:

$$dS = \frac{C_V}{T} dT \tag{2.13}$$

Integration of Eq. (2.13) yields

$$\Delta S = S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_V}{T} dT \qquad (2.14)$$

At $p = \text{const}$, Eq. (2.5) becomes

$$dS = \frac{C_p}{T} dT \qquad (2.15)$$

Integration of Eq. (2.15) gives

$$\Delta S = S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_p}{T} dT \qquad (2.16)$$

When integrating Eqs. (2.14) and (2.16), we must know the temperature dependence of the heat capacity at constant volume (C_V) and constant pressure (C_p) for the entire interval from T_1 to T_2. The change in entropy for an isothermal change in the state of aggregation at $p = \text{const}$, according to the analytic expression of the second law of thermodynamics [Eq. (2.1)], will be

$$\Delta S = S_2 - S_1 = \frac{1}{T} \int_1^2 \delta Q \qquad (2.17)$$

And since in the given case, the heat received by the system equals the heat of the change in the state of aggregation, i.e. $\int_1^2 \delta Q = Q_{\text{ph.tr}}$, then

$$\Delta S = S_2 - S_1 = \frac{Q_{\text{ph.tr}}}{T} \qquad (2.18)$$

where the subscript "ph.tr" stands for phase transition.

Equations (2.16) and (2.18) make it possible to calculate the change in entropy as a result of the isobaric transition of any substance from the solid state at T_1 to the gaseous (vapour) state at T_2:

$$\Delta S = \int_{T_1}^{T_m} \frac{C_p^c}{T} dT + \frac{\Delta H_f}{T_m} + \int_{T_m}^{T_b} \frac{C_p^{lq}}{T} dT + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T_2} \frac{C_p^g}{T} dT \qquad (2.19)$$

where C_p^c, C_p^{lq}, and C_p^g = heat capacities at constant pressure for the crystalline, liquid, and gaseous states of the substance being considered, respectively

ΔH_f and ΔH_{vap} = heats of fusion and vaporization, respectively

T_m and T_b = melting and boiling points, respectively.

Example 56. Calculate the change in entropy involved in heating to 50 °C one mole of a monatomic ideal gas which occupies a volume of 23.64 dm³ at 15 °C if its final volume is 26.51 dm³.

Solution. According to Eq. (2.7), we have

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For a monatomic ideal gas, we have $C_V = 2.98$ cal/mol·K. Hence,

$$\Delta S = 2.98 \times 2.303 \log \frac{323}{288} + 1.987 \times 2.303 \log \frac{26.51}{23.64} =$$
$$= 0.57 \text{ cal/mol} \cdot K$$

Example 57. Find the change in entropy when one mole of a diatomic ideal gas at a pressure of 5 atm is heated from 150 to 200 °C if the final pressure is 5.59 atm (the volume is constant).

Solution. From Eq. (2.8), we have

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2}$$

Hence,

$$\Delta S = 6.96 \times 2.303 \log \frac{473}{423} + 1.987 \times 2.303 \log \frac{5}{5.59} =$$
$$= 0.556 \text{ cal/mol} \cdot K$$

For a diatomic ideal gas, as we know from the kinetic theory of an ideal gas, $C_V = 5R/2 = 5 \times 1.987/2 = 4.968$ cal/mol·K. Therefore,

$$C_p = C_V + R = 4.968 + 1.987 \approx 6.96 \quad \text{cal/mol} \cdot K$$

Example 58. Two vessels having the same volume are separated from each other by a cock. One contains one mole of an ideal gas, and the other is empty. Find the change in entropy in the process which will occur after the cock is opened.

Solution. Since the process is isothermal, then by Eq. (2.9)

$$\Delta S = 2.303 \times 1.987 \log \frac{2}{1} = 1.375 \text{ cal/mol} \cdot K$$

Example 59. Find the change in entropy in the reversible isothermal compression of (1) one mole of oxygen from $p_1 = 0.001$ to $p_2 = 0.01$ atm; and (2) one mole of methane from $p_1 = 0.1$ to $p_2 = 1$ atm. Assume that the gases are ideal in both cases.

Solution. Using Eq. (2.10), we have

(1) $\Delta S = R \ln \left(\frac{p_1}{p_2} \right) = 1.987 \times 2.303 \log \frac{0.001}{0.01} =$
$$= -4.576 \text{ cal/mol} \cdot K$$

(2) $\Delta S = 1.987 \times 2.303 \log \frac{0.1}{1} = -4.576 \text{ cal/mol} \cdot K$

Example 60. Find the change in entropy when two moles of hydrogen expand from a volume of 30 dm³ under a pressure of 2 atm to a volume of 100 dm³ under a pressure of 1 atm. Assume that hydrogen is an ideal gas with $C_p = 7.4$ cal/mol·K

Solution. For n moles of an ideal gas, Eq. (2.11) giving the change in entropy is modified as follows:

$$\Delta S = nC_V \ln \frac{p_2 V_2^\gamma}{p_1 V_1^\gamma}$$

Considering that $C_p - C_V = R$ and $C_p/C_V = \gamma$, we transform the above equation to the sum of logarithms:

$$\Delta S = n \left(C_V \ln \frac{p_2}{p_1} + C_p \ln \frac{V_2}{V_1} \right)$$

Hence,

$$\Delta S = 2 \times 2.303 \left[(7.4 - 1.987) \log \frac{1}{2} + 7.4 \log \frac{100}{30} \right] = 10.3 \ \text{cal/K}$$

Example 61. Show that for a gas obeying the van der Waals equation the entropy of one mole will be expressed by

$$S = C_V \ln T + R \ln (V - b) + S_0$$

where S_0 is a constant of the equation.

Solution. The combined equation of the first and second laws of thermodynamics, according to Eq. (2.4), has the form

$$dS = \frac{l}{T} dV + \frac{C_V}{T} dT$$

The Clausius-Clapeyron equation can be used to determine l for a gas obeying the van der Waals equation:

(a) $l = T \left(\frac{\partial p}{\partial T} \right)_V$

We solve the van der Waals equation relative to p:

(b) $p = \frac{RT}{V - b} - \frac{a}{V^2}$

Differentiation of Eq. (b) yields

(c) $\left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{V - b}$

We compare Eqs. (a) and (c):

(d) $l = T \frac{R}{V - b}$

Thus, the entropy of a real gas according to Eq. (d) and the combined analytic expression of the first and second laws of thermoby-

namics has the form

(e) $dS = \dfrac{R}{V-b}\,dV + \dfrac{C_V}{T}\,dT$

Integration gives us the required expression for the entropy of one mole of a real gas obeying the van der Waals equation:

(f) $S = R \ln (V - b) + C_V \ln T + S_0$

Example 62. Show that when 250 cm³ of nitrogen and 500 cm³ of oxygen are mixed at a pressure of 800 mm Hg, the value of ΔS equals 0.04 cal/mol·K. Assume that both gases are ideal, and $T = 273$ K.

Solution. The change in entropy when ideal gases are mixed is determined by Eq. (2.12). The number of moles of nitrogen and oxygen can be calculated with the aid of the equation of state of an ideal gas: $n = pV/RT$:

$$n_{N_2} = \frac{250 \times 800}{10^3 \times 760 \times 0.082 \times 273} = 0.010\,43$$

$$n_{O_2} = \frac{800 \times 500}{10^3 \times 760 \times 0.082 \times 273} = 0.020\,86$$

Hence, the change in entropy as a result of mixing will be

$$\Delta S = 2.303 \times 1.987 \left(0.010\,43 \log \frac{750}{250} + 0.020\,86 \log \frac{750}{500} \right) =$$
$$= 0.04 \ \text{cal/K}$$

Example 63. One vessel contains 18 g of water vapour, and a second vessel having the same volume contains 40 g of argon. Determine the change in entropy when the gases are mixed as a result of communication of the vessels. Assume that the gases obey the laws of the ideal state.

Solution. The change in entropy as a result of mixing two different gases in isothermal conditions is

$$\Delta S = R \left(n_1 \ln \frac{V}{V_1} + n_2 \ln \frac{V}{V_2} \right)$$

Therefore

$$\Delta S = 2.303 \times 1.987 \ (1 \ \log 2 + 1 \ \log 2) = 2.754 \ \text{cal/K}$$

Example 64. Considering that C_p for nitrogen equals $7R/2$ and is constant when the temperature changes, calculate ΔS when 10 g of N_2 are heated from 0 to 100 °C (a) at constant pressure; and (b) at constant volume.

Solution. We use Eq. (2.16). According to the initial conditions, the change in entropy ΔS at $p =$ const will be

$$\Delta S = \frac{10}{28} \int\limits_{273}^{373} \frac{7R}{2} \frac{dT}{T} = \frac{10 \times 7 \times 1.987 \times 2.303}{28 \times 2} \log \frac{373}{273} = 0.774 \text{ cal/K}$$

and at $V =$ const

$$\Delta S = \frac{10}{28} \int\limits_{273}^{373} \left(\frac{7R}{2} - R\right) \frac{dT}{T} = \frac{10 \times 5 \times 1.987 \times 2.303}{28 \times 2} \log \frac{373}{273} =$$

$$= 0.55 \text{ cal/K}$$

Example 65. The temperature dependence of C_p within the interval from 298 to 1500 K for gaseous benzene is expressed by the equation

$$C_p = -8.10 + 112.78 \times 10^{-3} T - 71.31 \times 10^{-6} T^2$$

Find the change in entropy for one mole of benzene when it is heated from 300 to 1000 K.
Solution.

$$\Delta S = S_{T_2} - S_{T_1} = \int\limits_{T_1}^{T_2} C_p \frac{dT}{T}$$

$$\Delta S = S_{1000} - S_{300} = \int\limits_{T_1}^{T_2} (-8.10 + 112.78 \times 10^{-3} T - 71.31 \times$$

$$\times 10^{-6} T^2) \frac{dT}{T} = -8.10 \times 2.303 \log \frac{1000}{300} + 112.78 \times$$

$$\times 10^{-3} (1000 - 300) - \frac{71.31 \times 10^{-6}}{2} (1000^2 - 300^2) =$$

$$= -9.76 + 78.4 - 32.10 = +36.54 \text{ cal/mol} \cdot \text{K}$$

Example 66. Calculate ΔS for the vaporization of one mole of liquid ethyl chloride ($t_b = 12.3 \,°C$) if its heat of vaporization at the boiling point $\Delta H_{vap} = 90.0$ cal/g.
Solution. Since the vaporization of a liquid is a reversible isobaric process, then according to Eq. (2.18) for ethyl chloride (C_2H_5Cl) we have

$$\Delta S = S^g - S^{lq} = \frac{\Delta H_{vap}}{T_b}$$

The molecular weight of ethyl chloride is 64.51. Hence,

$$\Delta S = \frac{90 \times 64.51}{12.3 + 273.15} = 20.34 \text{ cal/mol} \cdot \text{K}$$

Example 67. Find ΔS for the process of transformation of 100 **g** of water taken at 0 °C into vapour at 120 °C. The heat of vaporization of water at 100 °C is 2258.4 kJ/kg. The specific heat capacities of water at $p =$ const for the liquid and gaseous states are 4.19 and 1.91 kJ/kg·K, respectively.

Solution. We use Eq. (2.19):

$$\Delta S = m \int_{T_1}^{T_b} C_p^{lq} \frac{dT}{T} + \frac{m\Delta H_{vap}}{T_b} + m \int_{T_b}^{T_2} C_p^g \frac{dT}{T}$$

whence

$$\Delta S = 100 \times 4.19 \times 2.303 \log \frac{373}{273} + \frac{100 \times 2258.4}{373} + 100 \times 1.91 \times$$

$$\times 2.303 \log \frac{393}{373} = 130.5 + 605.4 + 9.97 = 745.87 \quad \text{J/K}$$

Example 68. Find the change in entropy in the process of freezing of supercooled benzene at 268.15 K if at 278.15 K the molar heat of fusion $\Delta H_f = -9956 \times 10^3$ J/kmol·K, and the true molar heat capacities of liquid and crystalline benzene are 127.3×10^3 and 123.6×10^3 J/kmol·K, respectively. Also determine the direction of the process.

Solution. The process is clearly irreversible, consequently $\Delta S > > Q/T$. The change in entropy ΔS can be calculated only for a reversible process. Entropy, however, is a function of state that does not depend on the path of a process, but depends only on the initial and final states. If a reversible and an irreversible processes are conducted at the same initial and final states of a system, then $\Delta S_{rev} = \Delta S_{irrev}$. Any irreversible process can be mentally conducted in several steps in the same boundary conditions, and the entropy can be calculated for each reversible step. Therefore, the sum of the changes in entropy in these steps will equal the sum of the changes in entropy in the irreversible process. We shall, therefore, mentally conduct our process reversibly in three steps:

$$C_6H_6(lq, 268.15\ K, 1.01 \times 10^5\ N/m^2) \xrightarrow{\Delta S=?} C_6H_6(c, 268.15\ K, 1.01 \times 10^5\ N/m^2)$$

$$\downarrow \Delta S_1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad \uparrow \Delta S_3$$

$$C_6H_6(lq, 278.15\ K, 1.01 \times 10^5\ N/m^2) \xrightarrow{\Delta S_2} C_6H_6(c, 278.15\ K, 1.01 \times 10^5\ N/m^2)$$
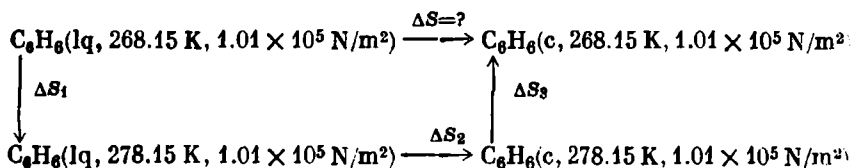
where 1.01×10^5 N/m^2 = 1 atm.

Hence, $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$, where

$$\Delta S_1 = \int_{268.15}^{278.15} 127.3 \times 10^3 \frac{dT}{T}, \quad \Delta S_2 = \frac{\Delta H_{273}^c}{278.15};$$

$$\Delta S_3 = \int_{278.15}^{268.15} 123.6 \times 10^3 \frac{dT}{T}$$

The value of ΔH^c at 268.15 K can be found by the Kirchhoff equation:

$$\Delta H_{268} = \Delta H_{278} + (C_p^c - C_p^{lq}) \Delta T$$

whence

$$\Delta H_{268} = -9956 \times 10^3 + (123.6 \times 10^3 - 127.3 \times 10^3)(-10) =$$
$$= -9912 \times 10^3 \text{ J/kmol}$$

Consequently, the change in entropy as a result of the process being considered will be

$$\Delta S = \int_{268.15}^{278.15} 127.3 \times 10^3 \frac{dT}{T} + \frac{\Delta H_{278}^c}{278.15} + \int_{278.15}^{268.15} 123.6 \times 10^3 \frac{dT}{T} =$$
$$= -35.62 \times 10^3 \text{ J/kmol·K}$$

The direction of the process can be determined according to the change in entropy in an isolated system. The amount of heat given up to the surroundings at 268.15 K was 9912×10^3 J; therefore, the entropy of the surroundings increased by $9912 \times 10^3/268.15 = 36.96 \times 10^3$ J/kmol·K, and as a whole the entropy of the system increased by $36.96 \times 10^3 - 35.62 \times 10^3 = 1.34 \times 10^3$ J/kmol·K. The plus sign of ΔS points to a spontaneous process.

Example 69. Using the value of ΔS from Example 68, find the saturated vapour pressure over supercooled liquid benzene at 268.15 K if the saturated vapour pressure of crystalline benzene at the same temperature is 17.1 mm Hg. Compare the result with the value found by the equation

$$\log p = 7.0664 - \frac{1298}{230 + t}$$

where p is in mm Hg, and t in °C.

Solution. We mentally conduct the process of freezing of benzene reversibly through the gaseous phase:

$$C_6H_6(g, 268.15\ K,\ p_{268}^{lq}) \xrightarrow{\Delta S_2} C_6H_6(g, 268.15\ K,\ p_{268}^{c})$$

$$\Big\downarrow \Delta S_1 \qquad\qquad\qquad \Big\uparrow \Delta S_3$$

$$C_6H_6(lq, 268.15\ K) \xrightarrow{\Delta S = ?} C_6H_6(c, 268.15\ K)$$
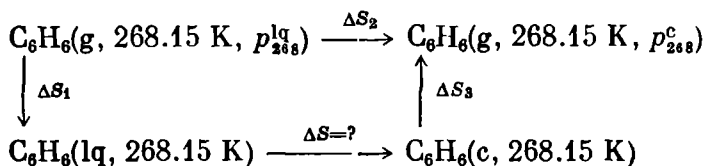
where p_{268}^{lq} and p_{268}^{c} are the saturated vapour pressures at 268.15 K over the supercooled liquid and crystalline benzene, respectively.

The change in entropy

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

and

$$\Delta S = \frac{\Delta H_{vap}}{268.15} + \left(-R \ln \frac{p_{268}^{c}}{p_{268}^{lq}}\right) + \frac{\Delta H_{subl}}{268.15} = -R \ln \frac{p_{268}^{c}}{p_{268}^{lq}} + \frac{\Delta H_t}{268.15}$$

In accordance with Example 68, we have

$$-35.62 = -8.31 \times 2.303 \log 17.1 + 8.31 \times 2.303 \log p_{268}^{lq} -$$

$$-\frac{9912}{268.15}$$

whence

$$\log p_{268}^{lq} = \frac{-35.62 + 8.31 \times 2.303 \times 1.233 + 36.96}{8.31 \times 2.303} = 1.3028$$

and $p_{268}^{lq} = 20.08$ mm Hg.

According to the equation given in the initial conditions, for $t = 268.15 - 273.15 = -5\ °C$, we have

$$\log p_{268}^{lq} = 7.0664 - \frac{1298}{230 - 5} = 1.2975$$

and the saturated vapour pressure of liquid benzene at 268.15 K will be $p_{268}^{lq} = 19.84$ mm Hg, which differs from the found value by 1.2%.

Example 70. The temperature dependence of the true molar heat capacity for gaseous *n*-heptane at $p = $ const for the temperature interval from 298 to 1500 K is given by the equation

$$C_p = 1.20 + 156.25 \times 10^{-3}T - 83.35 \times 10^{-6}T^2$$

Calculate the entropy of gaseous *n*-heptane at 500 K and atmospheric pressure if it equals 101.6 cal/mol·K at 298 K and the same pressure.

Solution. We use Eq. (2.16) to find the change in entropy as a result of heating one mole of n-heptane from 298 to 500 K:

$$\Delta S = S_{500} - S_{298} =$$

$$= \int_{298}^{500} (1.20 + 156.25 \times 10^{-3}T - 83.35 \times 10^{-6}T^2) \frac{dT}{T} =$$

$$= 1.20 \times 2.303 \log \frac{500}{298} + 156.25 \times 10^{-3} (500 - 298) -$$

$$- \frac{83.35 \times 10^{-6}}{2} (500^2 - 298^2) = 25.95 \text{ cal/mol} \cdot \text{K}$$

Consequently, since $\Delta S = S_{500} - S_{298}$, we have

$$S_{500} = \Delta S + S_{298} = 25.95 + 101.6 = 127.55 \text{ cal/mol} \cdot \text{K}$$

Example 71. Using the combined analytic expressions of the first and second laws of thermodynamics, derive the dependences of the entropy on volume and pressure at constant temperature.

Solution. Before finding the relationships $(\partial S/\partial V)_T$ and $(\partial S/\partial p)_T$, we shall recall certain properties of a total differential. If the function z is a property of a system determined by two other properties x and y, i.e. if $z = f(x, y)$, then the expression

(a) $dz = M \, dx + N \, dy$

in which M and N are also functions of x and y, is a total differential. And this means that

(b) $dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$

Comparing Eqs. (a) and (b), we get

(c) $M = \left(\frac{\partial z}{\partial x} \right)_y$ and $N = \left(\frac{\partial z}{\partial y} \right)_x$

Hence

(d) $\left(\frac{\partial M}{\partial y} \right)_x = \frac{\partial^2 z}{\partial y \cdot \partial x}$ and $\left(\frac{\partial N}{\partial x} \right)_y = \frac{\partial^2 z}{\partial x \cdot \partial y}$

Since derivatives do not depend on the sequence of differentiation, the first theorem on the total differential can be written as

(e) $\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$

Most thermodynamic processes occur in conditions of the constancy of one of the parameters. Therefore, wide use is made in thermodynamics of partial derivatives whose relationship is obtained as

follows. Equation (b), if $z = \text{const}$, becomes

$$\left(\frac{\partial z}{\partial x}\right)_y (\partial x)_z + \left(\frac{\partial z}{\partial y}\right)_x (\partial y)_z = 0$$

whence

(f) $\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x = 0$

Multiplying Eq. (f) by $(\partial y/\partial z)_x$, we get

(g) $\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$

Now we are ready to pass over to the solution of our problem. The combined analytic expressions of the first and second laws of thermodynamics (for reversible processes) can be presented in the form

(h) $dU = T\,dS - p\,dV$

(i) $dH = T\,dS - V\,dp$

Equation (g) as applied to the functional relationship $\varphi\,(T,\,V,\,S)$ has the form

(j) $\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = -1$

Applying the property of a total differential [see Eq. (e)] to Eq. (h), we get

(k) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

Combining the last equation with Eq. (j), we get the required dependence of the entropy on volume at $T = \text{const}$:

(l) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

The pressure dependence of the entropy at $T = \text{const}$ can be obtained by a similar procedure. For this purpose, Eq. (g) must be written for the relationship $\varphi\,(T,\,p,\,S) = 0$, and the property of a total differential applied to Eq. (i). After the corresponding transformations, we have

(m) $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

2.2
Calculation of Absolute Value of Entropy

Equations (2.16) and (2.19) considered above permit us to calculate the change in entropy as a result of the transition of a substance from one state to another. They cannot be used, however, to calculate

the absolute value of the entropy of a substance in the conditions being considered. Such a possibility is provided by a postulate formulated by M. Planck. According to Planck's postulate, the entropy of an individual crystalline substance at absolute zero equals zero:

$$S_0 = 0 \tag{2.20}$$

In accordance with Planck's postulate, Eq. (2.16) when integrated from 0 to T K for an ideal solid becomes

$$S_T - S_0 = \int_0^T \frac{C_p}{T}\, dT = \int_0^T C_p d \ln T$$

Bearing in mind that $S_0 = 0$, we have

$$S_T = \int_0^T \frac{C_p}{T}\, dT = \int_0^T C_p d \ln T \tag{2.21}$$

This expression is the basis for calculating the absolute value of the entropy of any substance at the temperature T. The absolute value of the entropy of a substance in the gaseous state at the temperature T, according to Eqs. (2.19) and (2.20), can be calculated using the equation

$$S_T = \int_0^{T_m} \frac{C_p^c}{T}\, dT + \frac{\Delta H_t}{T_m} + \int_{T_m}^{T_b} \frac{C_p^{lq}}{T}\, dT + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} \frac{C_p^g}{T}\, dT \tag{2.22}$$

This equation can also be used to calculate the entropy of a substance that is in the liquid state at the temperature being considered. In this case, the last two terms of the right-hand side of Eq. (2.22) are disregarded.

When a substance has more than one modification in the solid state, the corresponding terms are added to the right-hand side of Eq. (2.22)— the increase in the entropy upon transition of the first modification to the second, the increase in the entropy upon heating of the second modification, etc.

The integrals in Eq. (2.22), except for very low temperatures, are usually determined according to experimentally found relationships $C_p/T = \varphi\,(T)$ or $C_p = \psi\,(\ln T)$. The numerical value of the integrals is found by determining the area confined by the curve and the axis of abscissas within the interval of the corresponding temperatures. Figure 3 shows typical graphs of C_p/T against T, and C_p against $\ln T$ that are encountered in graphical integration.

The areas indicated above are measured in one of the following ways: (a) with a planimeter; (b) the graph is plotted on squared paper,
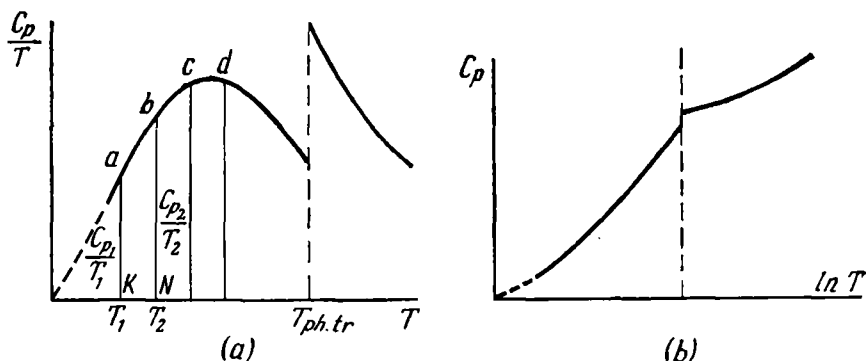
Fig. 3
Plotting of graphs for calculating the absolute value of the entropy by graphical integration

the number of squares in the area to be calculated is counted and divided by the area of one square; (c) the graph is glued onto a piece of cardboard, the area confined by the curve is cut out and weighed, and the weight obtained is compared with that of a unit of area; and (d) according to the trapezoid rule. We shall describe the latter rule, which is in the greatest favour.

The essence of this method is as follows. If it is necessary to find the area confined by a curve, for example by the one shown in Fig. 3a, the entire curve is divided into a number of segments so that each of them (*a-b*, *b-c*, *c-d*, etc.) is approximately a straight line. It is natural that the greater the number of trapezoids into which the area confined by a curve is divided, the more accurate will be the value of the area calculated by this method. The area of one trapezoid, for instance *abNK*, is equal to

$$0.5 \left(\frac{C_{p_1}}{T_1} + \frac{C_{p_2}}{T_2} \right) (T_2 - T_1)$$

The total area confined by the curve equals the sum of the areas of all the trapezoids.

Since the experimental values of $C_p = \varphi(T)$ are mainly known beginning only from 10 to 20 kelvins (when liquid hydrogen is used for cooling), it becomes necessary to divide the first term of Eq. (2.22) into two integrals. The first of them, taken from 0 K to the temperature at which the heat capacities are known, is found following the assumption that in this region the heat capacity, according to Debye's law, changes proportionally to the cube of the temperature:

$$C_p = aT^3 \tag{2.23}$$

where a is a constant of the [equation.

Since considerable difficulties are involved in the experimental measurement of the heat capacity at a very low temperature, especially near absolute zero, it was proposed to extrapolate the heat capacity to the region of low temperatures on the basis of data obtained above the temperature of liquid air ($T \approx 90$ K).

K. Kelley, G. Parks, and H. Huffman [57, 25] established the following temperature dependence of C_p:

$$C_p = (A + BT) C_p^\circ \qquad (2.24)$$

where C_p = true molar heat capacity of an organic substance at T K
C_p° = molar heat capacity of a hypothetic standard substance (its values for aliphatic and cyclic hydrocarbons from 20 to 90 K are given in Appendix 13)
A and B = constants of the equation.

Equation (2.24) allows us to calculate the entropy of any substance at 90 K:

$$S_{90}^\circ = \int_0^{90} \frac{C_p}{T} dT = \int_0^{90} \frac{(A+BT) C_p^\circ}{T} dT = A \int_0^{90} \frac{C_p^\circ}{T} dT + B \int_0^{90} C_p^\circ dT =$$

$$= AS_{90}^\circ + B \int_0^{90} C_p^\circ dT \qquad (2.25)$$

where S_{90}° is the entropy of the standard substance at 90 K. The values of S_{90}° and $\int_0^{90} C_p^\circ dT$ given in Appendix 13 were obtained by graphical integration within the interval from 20 to 90 K. The heat capacities were extrapolated to below 20 K with the aid of Eq. (2.23). A comparison of experimental data with the values calculated by the above method shows that the discrepancies do not exceed about 2.5%.

Example 72. Using the experimental data given below, calculate the entropy of liquid methyl cyclopentane at 298.15 K.

The molar heat of fusion of methyl cyclopentane is 1656 cal/mol.

Solution. According to Eq. (2.22), the entropy of liquid methyl cyclopentane at 298.15 K is

$$S_{298}^{lq} = \int_0^{130.73} \frac{C_p^c}{T} dT + \frac{\Delta H_f}{130.73} + \int_{130.73}^{298.15} \frac{C_p^{lq}}{T} dT$$

But since the heat capacity of methyl cyclopentane has been determined only down to 12 K, Debye's law (2.23) must be used for lower temperatures:

$$S_{298}^{lq} = \int_0^{12} \frac{aT^3}{T} dT + \int_{12}^{130.73} \frac{C_p^c}{T} dT + \frac{\Delta H_f}{130.73} + \int_{130.73}^{298.15} \frac{C_p^{lq}}{T} dT$$

T, K	C_p of solid substance, cal/mol·K	T, K	C_p of liquid substance, cal/mol·K
12	0.66	140	29.89
13	0.84	150	29.98
14	1.04	160	30.14
15	1.25	170	30.35
20	2.48	180	30.61
25	3.90	190	30.92
30	5.30	200	31.31
35	6.60	210	31.78
40	7.79	220	32.29
45	8.83	230	32.85
50	9.78	240	33.46
55	10.64	250	34.13
60	11.42	260	34.84
70	12.78	270	35.60
80	14.04	280	36.40
90	15.24	290	37.22
100	16.30	300	38.09
110	17.37		
120	18.44		
130	19.51		
130.73	M.p.		

We have assumed that the heat capacity of solid methyl cyclopentane within the interval from 0 to 12 K follows Debye's law. Therefore, the constant a can be found as follows. The value of C_p at 12 K equals 0.66. Hence,

$$0.66 = aT^3 = a \times 12^3 \quad \text{and} \quad a = \frac{0.66}{12^3}$$

We determine the first integral:

$$\Delta S_{0\text{-}12} = S_{12} - S_0 = \int_0^{12} \frac{C_p}{T} \, dT = \int_0^{12} \frac{aT^3}{T} \, dT = \int_0^{12} aT^2 \, dT$$

$$\Delta S_{0\text{-}12} = a \frac{T^3}{3} = a \frac{12^3}{3} = \frac{0.66}{12^3} \times \frac{12^3}{3} = 0.22 \text{ cal/mol·K}$$

The second and third integrals can be found by graphical integration. For this purpose, the experimentally found temperature dependences of the heat capacity are listed in Table 1 (p. 126) in the form $C_p/T = \varphi(T)$ or $C_p = \psi(\log T)$. The data of Table 1 are used to

plot graphs of $C_p/T = \varphi(T)$ and $C_p = \psi(\log T)$ (Figs. 4 and 5). Since the heat capacities of solid methyl cyclopentane at 130.73 and 298.15 K are unknown, they have been determined by extrapolation (the corresponding values are given in parentheses in Table 1). For example for solid methyl cyclopentane

$$C_{p,130.73} = \frac{C_{p,130} - C_{p,120}}{10} \times 0.7 + C_{p,130} =$$

$$= \frac{19.51 - 18.44}{10} \times 0.7 + 19.51 = 19.585$$
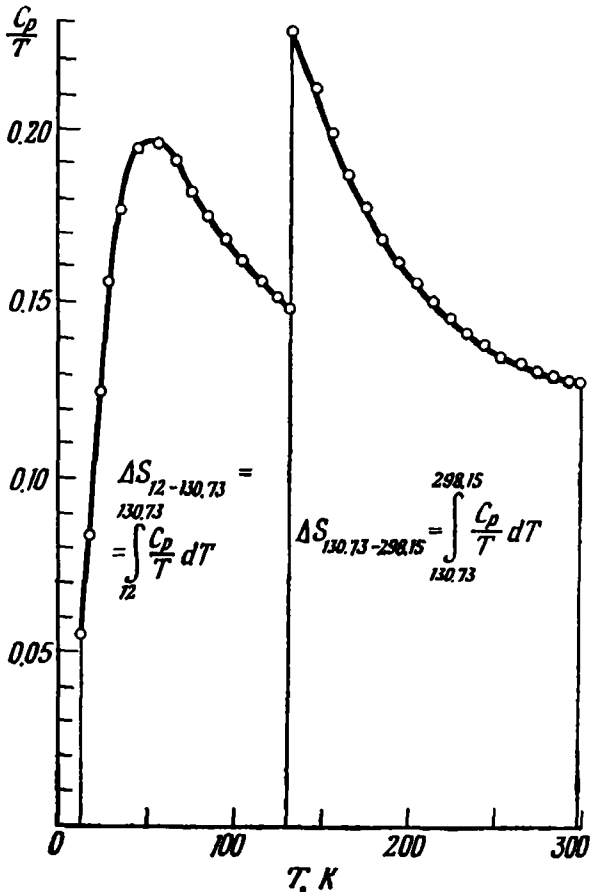
Fig. 4
Graph of C_p/T against T for methyl cyclopentane (Table 1, p. 126)

For liquid methyl cyclopentane at 130.73 and 298.15 K we have

$$C_{p,\,130.73} = C_{p,\,140} - \frac{C_{p,\,150} - C_{p,\,140}}{10} \times 9.3 =$$

$$= 29.89 - \frac{29.98 - 29.89}{10} \times 9.3 = 29.81$$

$$C_{p,\,298} = C_{p,\,290} + \frac{C_{p,\,300} - C_{p,\,290}}{10} \times 8.16 =$$

$$= 37.22 + \frac{38.09 - 37.22}{10} \times 8.16 = 37.93$$

We find the integrals by calculating the area under the corresponding curves, using the trapezoid rule for this purpose. When
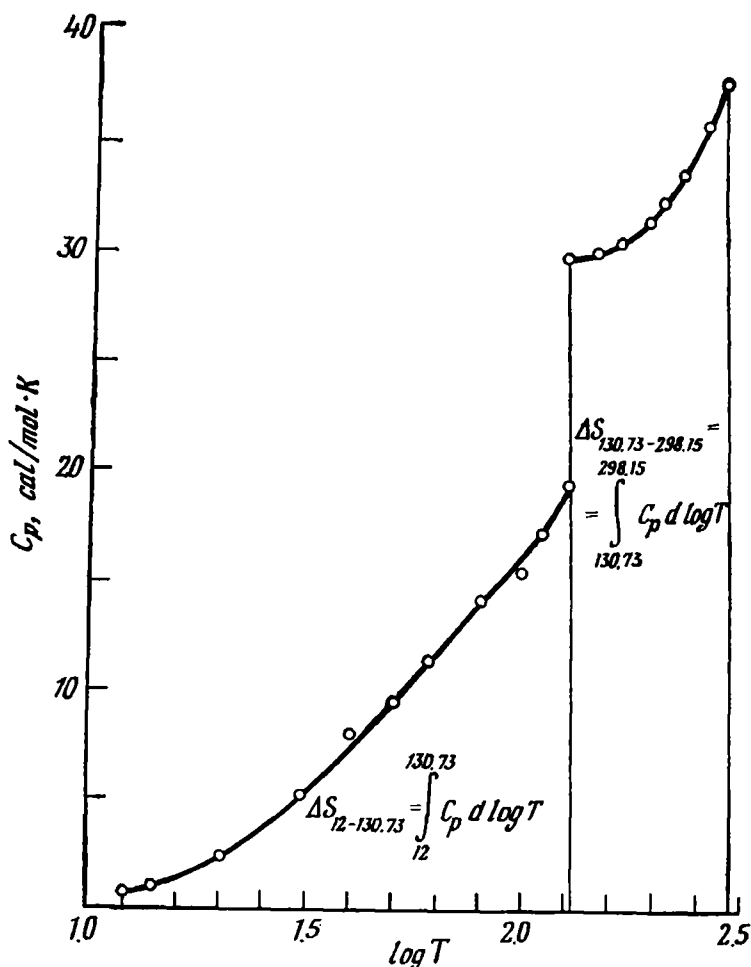
Fig. 5
Graph of C_p against log T for methyl cyclopentane (Table 1, p. 126)

considering the relationship $C_p/T = \varphi(T)$, we determine the integral $\int_{T_1}^{T_2} \frac{C_p}{T} dT$ as the area limited by the relevant curve of C_p/T against T (see Fig. 4). For instance for the interval from 20 to 25 K, we have

$$\Delta S = S_{25} - S_{20} = \frac{\frac{2.48}{20} + \frac{3.90}{25}}{2}(25 - 20) =$$

$$= \frac{0.124 + 0.156}{2}(25 - 20) = 0.700$$

The results have been entered in Table 1. Summation of the areas for the two integrands gives

$$\Delta S_{12\text{-}130.73} = \int_{12}^{130.73} \frac{C_p^c}{T} dT = 19.867 \text{ cal/mol} \cdot \text{K}$$

$$\Delta S_{130.73\text{-}298.15} = \int_{130.73}^{298.15} \frac{C_p^{lq}}{T} dT = 26.475 \text{ cal/mol} \cdot \text{K}$$

The change in entropy at the melting point is

$$\Delta S_{130.73} = \frac{\Delta H_{130.73}}{130.73} = \frac{1656}{130.73} = 12.667 \text{ cal/mol} \cdot \text{K}$$

The sum of the calculated values is

$$S_{298}^{lq} = \int_0^{12} \frac{C_p^c}{T} dT + \int_{12}^{130.73} \frac{C_p^c}{T} dT + \frac{\Delta H_f}{130.73} + \int_{130.73}^{298.15} \frac{C_p^{lq}}{T} dT =$$

$$= 0.22 + 19.867 + 12.667 + 26.475 = 59.229 \text{ cal/mol} \cdot \text{K}$$

Similar calculations can be performed on the basis of the graphical relationship $C_p = \psi(\log T)$. For this purpose, we compile Table 1 and plot a graph of C_p against $\log T$ (see Fig. 5).

TABLE 1

T, K	c_p	c_p/T	ΔS	$\log T$	$\Delta S/2.303$
12	0.66	0.055		1.0792	
			0.05980		0.026
13	0.84	0.065		1.1139	
			0.06945		0.0302
14	1.04	0.074		1.1461	
			0.07880		0.03435
15	1.25	0.083		1.1761	
			0.51805		0.233
20	2.48	0.124		1.3010	
			0.70000		0.309
25	3.90	0.156		1.3979	
			0.83250		
30	5.30	0.177		1.4771	
			0.91375		
35	6.60	0.188		1.5441	1.192
			0.95875		
40	7.79	0.195		1.6021	
			0.97750		
45	8.83	0.196		1.6530	
			0.97875		
50	9.79	0.195		1.6990	1.69
			0.99750		
55	10.64	0.193		1.7404	
			0.96000		
60	11.42	0.190		1.7782	
			1.86500		
70	12.78	0.182		1.8451	
			1.79050		3.08
80	14.04	0.176		1.9031	
			1.72550		
90	15.24	0.169		1.9542	
			1.66250		
100	16.30	0.163		2.0000	
			1.60000		
110	17.35	0.157		2.0414	
			1.55250		
120	18.44	0.153		2.0792	2.07
			1.51750		
130	19.51	0.150		2.1139	
			1.10900		
130.73	(19.58)	0.149		2.1160	

TABLE 1 (concluded)

T, K	c_p	c_p/T	ΔS	$\log T$	$\Delta S/2.303$
130.73	(29.81)	0.228		2.116	
			2.0506		
140	29.89	0.213		2.146	
			2.0625		2.64
150	29.98	0.199		2.176	
			1.9390		
160	30.14	0.188		2.204	
			1.8340		
170	30.35	0.178		2.231	
			1.7425		
180	30.61	0.170		2.255	
			1.6650		2.98
190	30.92	0.163		2.279	
			1.5965		
200	31.31	0.156		2.301	
			1.5390		
210	31.78	0.151		2.322	
			1.4895		
220	32.29	0.147		2.342	
			1.4460		
230	32.85	0.143		2.362	3.14
			1.4095		
240	33.46	0.139		2.380	
			1.3780		
250	34.13	0.136		2.398	
			1.3515		
260	34.84	0.134		2.415	
			1.3285		
270	35.60	0.132		2.431	
			1.3085		
280	36.40	0.130		2.447	2.74
			1.2915		
290	37.22	0.128		2.462	
			1.0430		
298.15	(37.93)	0.127		2.474	
300	38.09	—	—	—	—

According to Eq. (2.22), we have

$$S_{298}^{lq} = \int\limits_0^{12} \frac{C_p^c}{T} dT + 2.303 \int\limits_{12}^{130.73} C_p^c d \log T + \frac{\Delta H_f}{130.73} +$$

$$+ 2.303 \int\limits_{130.73}^{298.15} C_p^{lq} d \log T$$

We find the value of $\Delta S_{0\text{-}12}$ in the same way as in the preceding example:

$$\Delta S_{0\text{-}12} = \int\limits_0^{12} \frac{C_p}{T} dT = \int\limits_0^{12} \frac{aT^3}{T} dT = 0.22 \ \text{cal/mol} \cdot \text{K}$$

To calculate the second and third integrals, we divide the curve $C_p = \psi (\log T)$ into a number of approximately straight sections and determine the area of each of the trapezoids formed in this way. For example

$$\Delta S_{60\text{-}100} = 2.3 \times \frac{11.42 + 16.3}{2} (\log 100 - \log 60) =$$

$$= 2.3 \times \frac{27.72}{2} \times (2.000 - 1.778) = 3.08 \ \text{cal/mol} \cdot \text{K}$$

All the data needed for the calculations, the intermediate data, and the final results are given in Table 1.

$$\Delta S_{12\text{-}130.73} = 2.3 \int\limits_{12}^{130.73} C_p^c d \log T = 19.94 \ \text{cal/mol} \cdot \text{K}$$

$$\Delta S_{130.73\text{-}298.15} = 2.3 \int\limits_{130.73}^{298.15} C_p^{lq} d \log T = 26.45 \ \text{cal/mol} \cdot \text{K}$$

$$\Delta S_{130.73} = \frac{\Delta H_f}{130.73} = \frac{1656}{130.73} = 12.667 \ \text{cal/mol} \cdot \text{K}$$

The sum of the values obtained is

$$S_{298}^{lq} = \Delta S_{0\text{-}12} + \Delta S_{12\text{-}130.73} + \Delta S_{130.73} + \Delta S_{130.73\text{-}298.15} =$$

$$= 0.22 + 19.94 + 12.667 + 26.45 = 59.277 \approx 59.28 \ \text{cal/mol} \cdot \text{K}$$

Example 73. Calculate the absolute entropy of liquid aniline at 298.15 K using the following data [9]:

T, K	C_p, cal/mol·K	*T*, K	C_p, cal/mol·K
Crystals		*Liquid*	
93.5	11.92	276.7	44.49
99.8	12.41	285.8	44.72
107.7	13.11	298.15	45.57
118.6	14.11		
139.5	16.02		
159.9	18.16		
180.3	20.36		
200.2	22.80		
211.3	24.19		
220.3	25.17		
229.1	26.26		
236.3	27.31		

The molar heat of fusion of aniline at its melting point, 266.8 K, is 2522 cal/mol. Use the method proposed by Kelley, Parks, and Huffman in the calculations.

Solution. The required value of the entropy of liquid aniline at 298.15 K, according to Eq. (2.22), is

$$S_{298}^{lq} = \int\limits_{0}^{90} \frac{C_p^c}{T}\, dT + \int\limits_{90}^{266.8} \frac{C_p^c}{T}\, dT + \frac{\Delta H_f}{266.8} + \int\limits_{266.8}^{298.15} \frac{C_p^{lq}}{T}\, dT$$

We determine the value of the first integral by the method of extrapolation of the heat capacities considered above. It follows from the initial conditions of the problem that C_p at 90 and 120 K equals 11.63 and 14.24 cal/mol·K, respectively. Using Eq. (2.24) and Appendix 13, we get the simultaneous equations

$$11.63 = (A + 90B)\, 14.20$$

$$14.24 = (A + 120B)\, 16.90$$

By solving these equations, we get $A = 0.751$ and $B = 0.000\ 758$.

In accordance with Eq. (2.25), we have

$$S_{90} = AS_{90}^{\circ} + B \int_{0}^{90} C_p^{\circ} \, dT = 0.751 \times 13.7 + 0.000\,758 \times 697 =$$

$$= 10.29 + 0.53 = 10.82 \ \text{cal/mol} \cdot \text{K}$$

We use the graphical method to calculate the second and third integrals. We compute the relationship $C_p/T = f(T)$ from the available experimental data for $C = \varphi(T)$ and enter the results in a table.

T, K	c_p	c_p/T	ΔS	T, K	c_p	c_p/T	ΔS
	Crystals				*Liquid*		
90.0	11.63	0.1290		266.8	44.29	0.1660	
			0.449				1.458
93.5	11.92	0.1275		275.7	44.49	0.1614	
			0.793				1.605
99.8	12.41	0.1243		285.8	44.72	0.1565	
			0.972				1.919
107.7	13.11	0.1217		298.15	45.57	0.1526	
			1.310				
118.6	14.11	0.1190					
			2.650				
139.5	16.02	0.1150					
			2.330				
159.9	18.16	0.1134					
			2.310				
180.0	20.36	0.1130					
			2.660				
200.2	22.80	0.1140					
			1.270				
211.3	24.19	0.1145					
			1.020				
220.2	25.17	0.1140					
			1.020				
229.1	26.26	0.1145					
			0.830				
236.3	27.31	0.1154					
			3.570				
266.8	31.76	0.1190					

The change in entropy as a result of melting of the aniline at 266.8 K is

$$\Delta S_{266.8} = \frac{2522}{266.8} = 9.46 \text{ cal/mol·K}$$

We find the second and third integrals by graphical integration:

$$\Delta S_{90\text{-}266.8} = \int\limits_{90}^{266.8} \frac{C_p^c}{T} \, dT = 20.78 \text{ cal/mol·K}$$

$$\Delta S_{266.8\text{-}298.15} = \int\limits_{266.8}^{298.15} \frac{C_p^{lq}}{T} \, dT = 4.98 \text{ cal/mol·K}$$

The sum of the values obtained is the absolute entropy of liquid aniline at 298.15 K:

$$S_{298}^{lq} = 10.82 + 20.78 + 9.46 + 4.98 = 46.04 \text{ cal/mol·K}$$

The value given in [20] and [25] (45.8 cal/mol·K) is very close to he calculated one.

2.3
Standard Entropy at 298.15 K (S_{298}°)

It is customary practice to relate entropy, like the other thermodynamic functions, to the standard state of a substance. The absolute value of entropy in the standard state is denoted S_{298}°. The use of S_{298}° considerably simplifies calculations of chemical equilibrium. The values of S_{298}°, like those of $(\Delta H_{298}^{\circ})_{form}$ and $(\Delta G_{298}^{\circ})_{form}$, are given in tables of standard values of thermodynamic functions in many reference books [1-3, 5, 7-9, 16-35, 56], and for selected substances in Appendix 1.

As regards substances in the gaseous state in standard conditions, especially such very simple gases as hydrogen, oxygen, and nitrogen, the standard state at sufficiently high temperatures is close in its properties to that actually observed. For substances consisting of more complex molecules, however, the standard state may considerably differ from the observed one, and the existence of a vapour at 1 atm and 298.15 K may often even be impossible. Thus, if we can still agree that the vapour of isobutane ($t_b = -11.72 \,°C$ at 1 atm) in the standard state obeys the law of an ideal gas and can really exist at 25 °C and 1 atm in the form of a gas, then the vapour of benzene, whose saturated vapour pressure at 25 °C equals 42 mm Hg, cannot be compressed to 1 atm at this temperature because condensation inevitably begins (at 25 °C and 42 mm Hg). We nevertheless often have to deal with such hypothetic processes in our calculations,

for example with the compression of a saturated vapour above the saturation pressure.

Equation (2.22) is generally used to calculate S_{298}°. This equation permits us to calculate the entropy of a real gas S_T at the temperature T and a pressure of 1 atm if vaporization was conducted at the normal boiling point. But to obtain the absolute value of the standard entropy $(S_T^\circ)^g$ [including $(S_{298}^\circ)^g$], we must introduce a correction taking into account the deviation of the real state of a gas from the ideal one. The equation for calculating this correction is obtained by combining the equation of state of the real gas with an equation giving the pressure dependence of the entropy at constant temperature:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{2.26}$$

For example, if we choose the Berthelot equation as the equation of state of the real gas, the correction will be

$$\frac{27}{32}\frac{RT_{cr}^3 p}{T^3 p_{cr}}$$

In this case, the standard entropy of a substance in the gaseous state at any temperature $(S_T^\circ)^g$ can be calculated as follows:

$$(S_T^\circ)^g = S_T^g + \frac{27RT_{cr}^3 p}{32T^3 p_{cr}} \tag{2.27}$$

where S_T^g = absolute value of entropy of a real gas calculated by Eq. (2.22)

$\quad\quad p$ = 1 atm (the standard state)

$\quad\quad T$ = temperature, K

p_{cr} and T_{cr} = critical pressure and temperature of the substance being considered, respectively

$\quad\quad R$ = molar gas constant equal to 1.987 cal/mol·K.

The correction expressed by the second term in Eq. (2.27) is of the order of magnitude of 0.1 cal/mol·K, as a rule, and is disregarded in approximate calculations.

When the entropy of a substance in the liquid or solid state at 25 °C is known, the standard entropy $(S_{298}^\circ)^g$ is calculated by the equation

$$(S_{298}^\circ)^g = S_{298}^{lq} + \frac{(\Delta H_{vap})_{298}}{298.15} + \frac{27T_{cr}^3 p_{298}}{32 \times 298.15^3 p_{cr}} - R \ln \frac{1}{p_{298}} \tag{2.28}$$

where $(\Delta H_{vap})_{298}$ = molar heat of vaporization of the liquid substance at 298.15 K

$\quad\quad p_{298}$ = saturated vapour pressure of the liquid substance at 298.15 K

$\quad\quad S_{298}^{lq}$ = absolute value of the entropy of the liquid substance determined by Eq. (2.22).

Example 74. Calculate the standard entropy of ethylene (gas) knowing the temperatures and heats of its phase transitions, its critical temperature and pressure, and also having the temperature dependence of the true molar heat capacity given below [3]:

T, K	C_p, cal/mol·K	T, K	C_p, cal/mol·K	T, K	C_p, cal/mol·K
15	0.682	80	11.55	120	16.32
20	1.519	85	12.35	130	16.21
25	2.537	90	13.29	140	16.12
30	3.559	95	14.73	150	16.07
35	4.682	98.1	16.03	160	16.04
40	5.665	100	17.05	169.4***	3237****
45	5.542	101.4	17.97	179.6	8.786
50	7.394	102.3	18.59	192.8	8.807
55	8.211	103.0	19.62	210.8	8.930
60	8.923	103.6	20.58	231.4	9.177
65	9.553	103.9*	800.8**	250.9	9.464
70	10.18	105	16.54	272.1	9.910
75	10.83	110	16.46	293.5	10.337

$*T_m = 103.9$ K; $**(\Delta H_f)_{103.9} = 800.8$ cal/mol; $***T_b = 169.4$ K; $****(\Delta H_{vap})_{169.4} = 3237$ cal/mol.

The critical temperature and pressure of ethylene are 283 K and 50.9 atm, respectively [7].

Solution. The entropy of gaseous ethylene, by Eq. (2.22), is

$$S^g_{298} = \int_0^{15} \frac{C_p^c}{T}\, dT + \int_{15}^{103.9} \frac{C_p^c}{T}\, dT + \frac{\Delta H_t}{T_m} + \int_{103.9}^{169.4} \frac{C_p^{lq}}{T}\, dT +$$

$$+ \frac{\Delta H_{vap}}{T_b} + \int_{169.4}^{298.15} \frac{C_p^g}{T}\, dT$$

We use Debye's law, $C_p = aT^3$, to calculate the first integral in the above expression. We first determine the constant of the equation. Since at 15 K we have $C_p = 0.682$, then

$$0.682 = aT^3 = a \times 15^3 \quad \text{and} \quad a = \frac{0.682}{15^3}$$

Knowing a, we find the first integral:

$$\Delta S_{0\text{-}15} = S_{15} - S_0 = \int_0^{15} \frac{C_p}{T}\, dT = \int_0^{15} \frac{aT^3}{T}\, dT = \int_0^{15} aT^2\, dT =$$

$$= a\frac{T^3}{3} = \frac{0.682}{15^3} \times \frac{15^3}{3} = 0.227 \text{ cal/mol·K}$$

TABLE 2

T	C_p/T	T	C_p/T	T	C_p/T
15	0.0454	80	0.1445	120	0.1361
20	0.0760	85	0.1455	130	0.1250
25	0.1015	90	0.1475	140	0.1152
30	0.1187	95	0.1550	150	0.1070
35	0.1340	98.1	0.1632	160	0.1000
40	0.1390	100	0.1705	160.4	0.0940
45	0.1430	101.4	0.1772	179.6	0.0489
50	0.1475	102.3	0.1822	192.8	0.0456
55	0.1492	103.0	0.1905	210.8	0.0423
60	0.1487	103.6	0.1985	231.4	0.0397
65	0.1470	103.9	0.2050	250.9	0.0379
70	0.1455	105	0.1578	272.1	0.0364
75	0.1445	110	0.1495	293.5	0.0353

After plotting a graph in the coordinates C_p/T against T, we find the remaining terms by graphical integration. For this purpose. we use the heat capacities given in the initial conditions to calculate $C_p/T = \varphi(T)$ (see Table 2) and plot the graph of this relationship shown in Fig. 6. By the method of graphical integration, we find

$$\Delta S_{15-103.9} = \int_{15}^{103.9} \frac{C_p^c}{T} dT = 12.21 \text{ cal/mol} \cdot \text{K}$$

$$\Delta S_{103.9-169.4} = \int_{103.9}^{169.4} \frac{C_p^{lq}}{T} dT = 7.91 \text{ cal/mol} \cdot \text{K}$$

$$\Delta S_{169.4-298.15} = \int_{169.4}^{298.15} \frac{C_p^g}{T} dT = 5.12 \text{ cal/mol} \cdot \text{K}$$

The change in entropy as a result of the phase transitions, by Eq. (2.18), is

$$\Delta S_m = \frac{800.8}{103.9} = 7.70 \text{ cal/mol} \cdot \text{K}$$

$$\Delta S_{vap} = \frac{3237}{169.4} = 19.11 \text{ cal/mol} \cdot \text{K}$$

Summation of all the values of ΔS yields

$$S_{298}^g = 0.227 + 12.21 + 7.70 + 7.91 + 19.11 + 5.12 =$$
$$= 52.277 \text{ cal/mol} \cdot \text{K}$$

The value obtained is the entropy of ethylene in the state of a real gas.

To get the standard entropy of gaseous ethylene in the state of an ideal gas, we have to add a correction to the obtained value of S_{298}^g. From Eq. (2.27), we have

$$(S_{298}^\circ)^g = S_{298}^g + \frac{27RT_{cr}^3 p_{298}}{32T^3 p_{cr}}$$

where the second term of the right-hand side of the equation is this correction.

Knowing the critical parameters of ethylene, we find

$$(S_{298}^\circ)^g = 52.277 + \frac{27 \times 1.987 \times 283^3 \times 1}{32 \times 169.4^3 \times 50.9} =$$

$$= 52.277 + 0.15 = 52.427 \text{ cal/mol·K}$$

Thus, the obtained value equals the entropy of ethylene in the state of an ideal gas (298.15 K and 1 atm). The tabulated value [20] is 52.45 cal/mol·K.
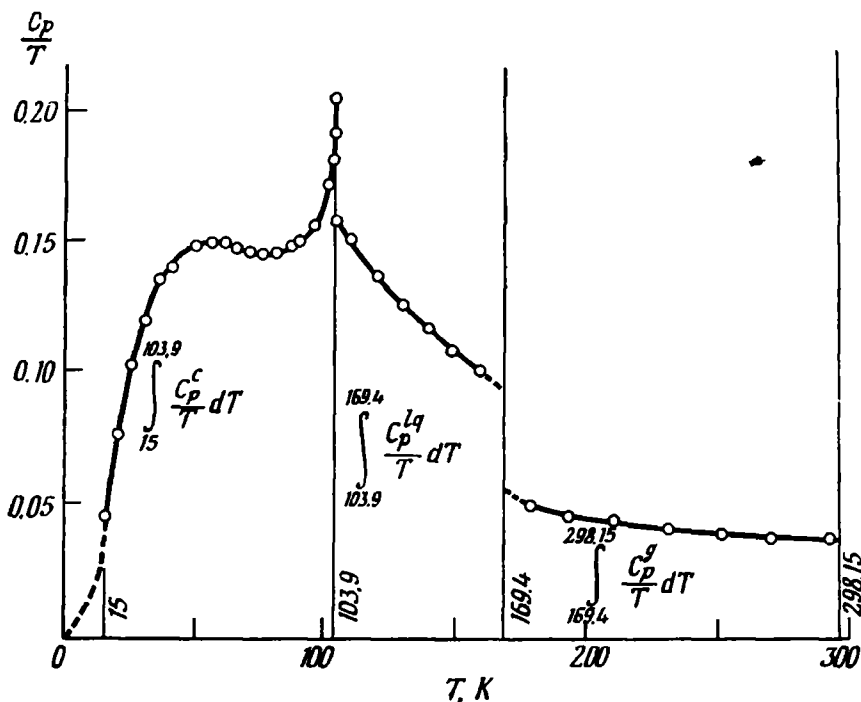
Fig. 6
Graphical method of calculating the entropy of ethylene (Example 74)

Example 75. In Example 72, we found that S_{298}^{lq} for methyl cyclopentane equals 59.25 cal/mol·K. Find the standard entropy of gaseous methyl cyclopentane at 298.15 K if the temperature dependence of the saturated vapour pressure of liquid methyl cyclopentane within the interval from —60 to +125 °C is expressed by the equation

$$\log p = 6.862\,83 - \frac{1186.06}{T - 47.12}$$

and the critical parameters are $T_{cr} = 532.8$ K and $p_{cr} = 37.4$ atm.

Solution. If the entropy of liquid methyl cyclopentane at 298.15 K is known, the standard entropy of gaseous methyl cyclopentane can be calculated by Eq. (2.28).

To solve the problem, we must know the saturated vapour pressure of liquid methyl cyclopentane at 298.15 K and its molar heat of vaporization at the same temperature. We determine the saturated vapour pressure of liquid methyl cyclopentane at 298.15 K:

$$\log p = 6.862\,83 - \frac{1186.06}{298.15 - 47.12} = 2.143$$

and

$$p_{298} = 139 \text{ mm Hg}$$

We use the Clausius-Clapeyron equation to determine the heat of vaporization $(\Delta H_{vap})_{298}$:

$$\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

Substituting a natural logarithm for the common one and introducing values, we get

$$\ln p = 2.303 \times 6.862\,83 - \frac{2.303 \times 1186.06}{T - 47.12} = 15.8 - \frac{2712}{T - 47.12}$$

Differentiation yields

$$\frac{d \ln p}{dT} = \frac{2712}{(T - 47.12)^2}$$

Hence,

$$\frac{\Delta H_{vap}}{RT^2} = \frac{d \ln p}{dT} = \frac{2712}{(T - 47.12)^2}$$

and

$$\Delta H_{vap} = \frac{2712 RT^2}{(T - 47.12)^2}$$

For $T = 298.15$ K we have

$$(\Delta H_{vap})_{298} = \frac{2712 \times 1.987 \times 298.15^2}{(298.15 - 47.12)^2} = 8650 \text{ cal/mol}$$

We use Eq. (2.28) to find the standard entropy of gaseous methyl cyclopentane at 298.15 K:

$$(S^\circ_{298})^g = 59.25 + \frac{8650}{298.15} + \frac{27 \times 1.987 \times 532.8^3 \times 139}{32 \times 298.15^3 \times 760 \times 37.4} -$$

$$- 2.303 \times 1.987 \log \frac{760}{139} = 59.25 + 29.00 + 0.0465 - 3.38 =$$

$$= 84.92 \text{ cal/mol} \cdot \text{K}$$

The tabulated value is $(S^\circ_{298})^g = 81.24$ cal/mol·K [20].

The difference of 3.68 cal/mol·K between the calculated value and the most authentic tabulated one can be explained by the inaccuracy of the Clausius-Clapeyron equation which causes an error in determining $(\Delta H_{vap})_{298}$.

2.4

Some Approximate Methods for Calculating the Standard Entropy at 298.15 K

The values of the standard entropy for a great number of substances made possible the discovery of certain laws that permit us to predict the entropy of unstudied substances. This, in turn, allows us to calculate the equilibria of chemical reactions without having to resort to the direct measurement of equilibrium and time-consuming calorimetric investigations at low temperatures. We shall consider some methods for calculating the standard entropy of organic and inorganic compounds.

Organic Compounds. 1. To determine S°_{298} for organic compounds in the state of an ideal gas, we can use the approximate method of introducing corrections (contributions) for the substitution of hydrogen by —CH_3 and other groups proposed by J. Anderson, G. Beyer, and K. Watson [44-46] and considered in detail in Chap. 1. The data needed for the calculations are given in Appendix 7. This method usually gives a discrepancy from experimental data of not over 2 cal/mol·K.

2. The standard entropy at 25 °C for gaseous normal paraffin hydrocarbons can be calculated by the equation proposed by R. Ewell [3, 58]:

$$\left.\begin{array}{l} S^\circ_{298} = 142.3 + 41.8n \text{ J/mol} \cdot \text{K} \\ S^\circ_{298} = 34.0 + 10.0n \text{ cal/mol} \cdot \text{K} \end{array}\right\} \tag{2.29}$$

where n is the number of carbon atoms in a hydrocarbon molecule.

The deviations of the values calculated by Eq. (2.29) from experimental data reach 4 to 8 cal/mol·K, and of the values obtained from spectral data 5 cal/mol·K, which is quite acceptable.

The standard entropy at 25 °C for liquid paraffin hydrocarbons (including hydrocarbons with a branched chain), cyclic, and aromatic hydrocarbons (including compounds with side chains) can be determined according to the equation proposed by G. Parks and H. Huffman [3, 8, 27]:

$$\left.\begin{aligned}(S_{298}^{\circ})^{\text{lq}} &= 104.60 + 32.22n - 18.33\,(r-2) + \\ &+ 81.59p_1 + 110.88p_2 \ \text{J/mol·K} \\ (S_{298}^{\circ})^{\text{lq}} &= 25.0 + 7.7n - 4.5\,(r-2) + 19.5p_1 + \\ &+ 26.5p_2 \ \text{cal/mol·K}\end{aligned}\right\} \tag{2.30}$$

where n = total number of carbon atoms outside a ring

$\quad\quad p_1$ = number of phenyl groups

$\quad\quad p_2$ = number of saturated rings (of cyclopentane or cyclohexane)

$\quad\quad r$ = number of branches on the straight chain or number of hydrocarbon groups (aliphatic, aromatic, cyclic) attached to a carbon atom of an aliphatic chain.

Equation (2.30) gives results considerably differing from experimental data. Consequently, it can be recommended only for an approximate assessment of S_{298}°.

Parks and Huffman [3, 27] proposed to use the following equation for calculating the standard entropy of solid normal paraffin hydrocarbons at 25 °C:

$$\left.\begin{aligned}(S_{298}^{\circ})^{\text{c}} &= 75.31 + 24.27n \ \text{J/mol·K} \\ (S_{298}^{\circ})^{\text{c}} &= 18.0 + 5.8n \ \text{cal/mol·K}\end{aligned}\right\} \tag{2.31}$$

where n is the number of carbon atoms in a molecule.

3. The equations proposed by I. Strelkov [18] can be used for an approximate assessment of S_{298}° for organic substances in the solid and liquid states:

$$\left.\begin{aligned}(S_{298}^{\circ})^{\text{c}} &= 4.6C_p^{\circ} \ \text{J/mol·K} \\ (S_{298}^{\circ})^{\text{c}} &= 1.1C_p^{\circ} \ \text{cal/mol·K}\end{aligned}\right\} \tag{2.32}$$

$$\left.\begin{aligned}(S_{298}^{\circ})^{\text{lq}} &= 5.9C_p^{\circ} \ \text{J/mol·K} \\ (S_{298}^{\circ})^{\text{lq}} &= 1.4C_p^{\circ} \ \text{cal/mol·K}\end{aligned}\right\} \tag{2.33}$$

where C_p° is the true molar heat capacity of the solid or liquid organic compound at $p = \text{const}$ and 25 °C.

4. The method proposed by P. Maslov [47–50] and described in Chap. 1 can be used to calculate S_{298}° for any halogen derivatives

of methane and ethane in the gaseous state. The data needed for determining S_{298}° for the halogen derivatives of methane with the aid of Eqs. (1.47-1.50) are given in Appendix 8. According to P. Maslov, the accuracy of the method depends on that of the initial thermodynamic properties of the compounds needed to calculate S_{298}°.

Inorganic Compounds. The following approximate methods proposed by R. Wenner [59] can be recommended for calculating the standard entropies of inorganic substances at 25 °C.

1. For solids

$$S_{298}^\circ = A \log M + B \tag{2.34}$$

where M = molecular weight of a compound
A and B = constants characteristic for each kind of compound.
Each kind of oxide (MeO, Me_2O_3, MeO_2, etc.) has its own values of A and B that are determined according to the known entropies of two substances of the given kind. The values of A and B for some kinds of compounds are given in Appendix 14.

2. For gaseous substances

$$\log S_{298}^\circ = A \log M + \log B \tag{2.35}$$

$$S_{298}^\circ = BM^A \tag{2.36}$$

where M = molecular weight of a gas
A and B = constants depending on the number of atoms in a molecule of the gas.
The values of A and B for selected gases are given in Appendix 15.

Example 76. Determine S_{298}° for gaseous methyl cyclopentane by the method of introducing corrections for the substitution of hydrogen by $-CH_3$ groups. Compare the result with the tabulated value equal to $(S_{298}^\circ)^g = 81.24$ cal/mol·K [20].
Solution.

$$S_{298}^\circ = 70.0 \qquad \Delta S_{298}^\circ = 11.5$$
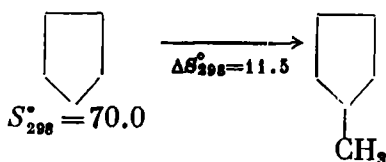
Summation yields

$$S_{298}^\circ = 70.0 + 11.5 = 81.5 \text{ cal/mol·K}$$

The relative error is $(0.26/81.5) \times 100 = 0.32\%$.

Example 77. Use the method of introducing corrections to calculate S_{298}° for gaseous acetone.

Solution.

$$CH_4 \xrightarrow[10.4]{} CH_3 - CH_3 \xrightarrow[9.8]{(A)=1,\ (B)=1}$$

$$\rightarrow CH_3 - CH_2 - CH_3 \xrightarrow[5.8]{(A)=2,\ (B)=1}$$

$$S^{\circ}_{298} = 44.5$$

$$\rightarrow CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_3 \xrightarrow[2.7]{(A)=3,\ (B)=1} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 \xrightarrow[-2.4]{} \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} = O$$
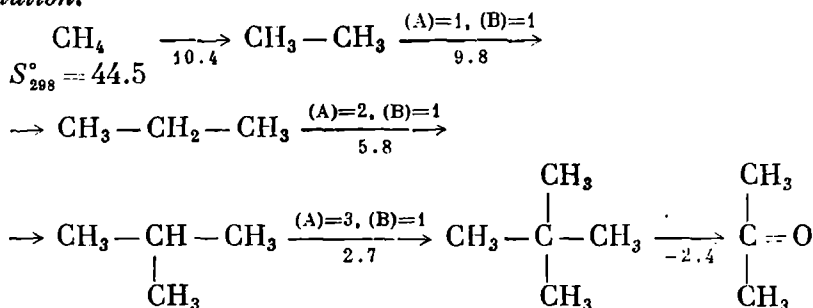
Summation of the entropy of the main group and the corrections for the substitution of hydrogen by —CH_3 and other groups gives

$$S^{\circ}_{298} = 44.5 + 10.4 + 9.8 + 5.8 + 2.7 - 2.4 = 70.8 \text{ cal/mol} \cdot K$$

According to published data [20], $(S^{\circ}_{298})^g = 70.5$ cal/mol·K.

Example 78. Calculate S°_{298} for gaseous 2,3-dimethylhexane and compare it with the value of 105.9 cal/mol·K given in [20]. Use the method of introducing corrections for substitution of hydrogen by —CH_3 groups in the calculations.

Solution.

$$CH_4 \xrightarrow[10.4]{} CH_3 - CH_3 \xrightarrow[9.8]{(A)=1,\ (B)=1}$$

$$S^{\circ}_{298} = 44.5$$

$$\rightarrow CH_3 - CH_2 - CH_3 \xrightarrow[9.2]{(A)=1,\ (B)=2}$$

$$\rightarrow CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow[9.2]{(A)=1,\ (B)=2}$$

$$\rightarrow CH_3 - CH_2 - CH_2 - CH_2 - CH_3 \xrightarrow[9.2]{(A)=1,\ (B)=2}$$

$$\rightarrow CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \xrightarrow[7.0]{(A)=2,\ (B)=2}$$

$$\rightarrow CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - CH_2 - CH_3 \xrightarrow[6.3]{(A)=2,\ (B)=3}$$

$$\rightarrow CH_3 - \underset{\underset{H_3C}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - CH_3$$
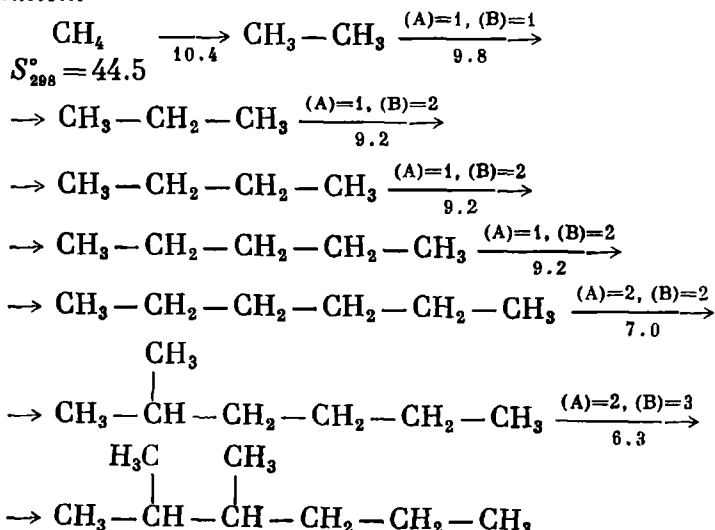
The sum is

$$(S^{\circ}_{298})^g = 44.5 + 10.4 + 9.8 + 9.2 + 9.2 + 9.2 + 7.0 +$$
$$+ 6.3 = 105.6 \text{ cal/mol} \cdot K$$

The similarity of the results should be considered as very good.

Example 79. Using Eq. (2.29), calculate $(S^\circ_{298})^g$ for *n*-butane.
Solution. Since $n = 4$, then

$$(S^\circ_{298})^g = 34.0 + 10.0 \times 4 = 74.0 \text{ cal/mol} \cdot \text{K}$$

The tabulated value is 74.1 cal/mol·K [20].

Example 80. Determine $(S^\circ_{298})^{lq}$ for triphenylmethane.
Solution. We use Eq. (2.30). For triphenylmethane

$$C_6H_5$$
$$|$$
$$C_6H_5 - CH - C_6H_5$$
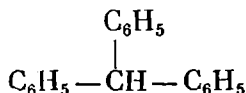
we have $n = 1$, $r = 3$, $p_1 = 3$, and $p_2 = 0$. Hence,

$$(S^\circ_{298})^{lq} = 25.0 + 7.7 \times 1 - 4.5 \times 1 + 19.5 \times 3 = 86.7 \text{ cal/mol} \cdot \text{K}$$

Example 81. Using Eq. (2.30), determine $(S^\circ_{298})^{lq}$ for tertiary butylbenzene.
Solution. For this compound we have $n = 4$, $r = 4$, $p_1 = 1$, and $p_2 = 0$. Hence,

$$(S^\circ_{298})^{lq} = 25.0 + 7.7 \times 4 - 4.5 \times 2 + 19.5 \times 1 = 84.3 \text{ cal/mol} \cdot \text{K}$$

Example 82. Find $(S^\circ_{298})^c$ for *n*-octadecane.
Solution. We use Eq. (2.31) to determine $(S^\circ_{298})^c$. For *n*-$C_{18}H_{38}$ we have $n = 18$. Therefore,

$$(S^\circ_{298})^c = 18.0 + 5.8 \times 18 = 122.4 \text{ cal/mol} \cdot \text{K}$$

Example 83. Assess the value of $(S^\circ_{298})^{lq}$ for *n*-heptane at 25 °C if its true molar heat capacity at constant pressure $(C^\circ_{p,\,298})^{lq}$ equals 53.7 cal/mol·K.
Solution. The standard entropy of organic substances in the liquid state is approximately assessed with the aid of Eq. (2.33), according to which

$$(S^\circ_{298})^{lq} = 1.4 C^\circ_p = 1.4 \times 53.7 = 75.20 \text{ cal/mol} \cdot \text{K}$$

The tabulated value of $(S^\circ_{298})^{lq}$ is 78.4 cal/mol·K [20]. Consequently, the relative error in the quantity determined in this way in comparison with the tabulated value is $(3.2/78.4) \times 100\% = 4.1\%$.

Example 84. Use Eq. (2.32) to calculate $(S^\circ_{298})^c$ for diphenyl if $(C_{p,\,298})^c = 46.6$ cal/mol·K for this compound.
Solution. According to Eq. (2.32)

$$(S^\circ_{298})^c = 1.1 (C^\circ_{p,\,298})^c = 1.1 \times 46.6 = 51.2 \text{ cal/mol} \cdot \text{K}$$

The tabulated value of $(S^\circ_{298})^c$ is 49.2 cal/mol·K.

Example 85. Using Maslovs' method, derive equations for determining the standard entropies of all halogen derivatives of methane in the gaseous state at 25 °C.

Solution. Letting X, Y, Z, and P stand for any halogen atom or hydrogen, we can conditionally write the possible halogen derivatives of methane as CX_2YZ, $CXYZP$, CX_3Y, and CX_2Y_2. In accordance with Eqs. (1.46) and (1.47), the entropy for the indicated substances can be determined with the aid of the following expressions:

(a) $S^\circ_{CX_2YZ} = \dfrac{1}{2}(S^\circ_{CX_2Y_2} + S^\circ_{CX_2Z_2}) -$

$- \dfrac{R}{4}(\ln D_{CX_2Y_2} + \ln D_{CX_2Z_2} - 2\ln D_{CX_2YZ}) -$

$- \dfrac{3R}{4}(\ln M_{CX_2Y_2} + \ln M_{CX_2Z_2} - 2\ln M_{CX_2YZ}) +$

$+ \dfrac{R}{2}(\ln \sigma_{CX_2Y_2} + \ln \sigma_{CX_2Z_2} - 2\ln \sigma_{CX_2YZ})$

(b) $S^\circ_{CXYZP} = \dfrac{1}{3}(S^\circ_{CXY_3} + S^\circ_{CXZ_3} + S^\circ_{CXP_3}) -$

$- \dfrac{R}{6}(\ln D_{CXY_3} + \ln D_{CXZ_3} + \ln D_{CXP_3} - 3\ln D_{CXYZP}) -$

$- \dfrac{R}{2}(\ln M_{CXY_3} + \ln M_{CXZ_3} + \ln M_{CXP_3} - 3\ln M_{CXYZP}) +$

$+ R(\ln \sigma_{CXZ_3} - \ln \sigma_{CXYZP})$

(c) $S^\circ_{CX_3Y} = \dfrac{1}{2}(S^\circ_{CX_4} + S^\circ_{CX_2Y_2}) -$

$- \dfrac{R}{4}(\ln D_{CX_4} + \ln D_{CX_2Y_2} - 2\ln D_{CX_3Y}) -$

$- \dfrac{3R}{4}(\ln M_{CX_4} + \ln M_{CX_2Y_2} - 2\ln M_{CX_3Y}) +$

$+ \dfrac{R}{2}(\ln \sigma_{CX_4} + \ln \sigma_{CX_2Y_2} - 2\ln \sigma_{CX_3Y})$

And, finally, for halogen derivatives of methane of the kind CX_2Y_2, we have

(d) $S^\circ_{CX_2Y_2} = \dfrac{1}{2}(S^\circ_{CX_4} + S^\circ_{CY_4}) -$

$- \dfrac{R}{4}(\ln D_{CX_4} + \ln D_{CY_4} - 2\ln D_{CX_2Y_2}) -$

$- \dfrac{3R}{4}(\ln M_{CX_4} + \ln M_{CY_4} - 2\ln M_{CX_2Y_2}) + R(\ln \sigma_{CX_4} - \ln \sigma_{CX_2Y_2})$

In these expressions D_i, M_i, and σ_i are the product of the principal moments of inertia, the molecular weight, and the symmetry number

of the halogen derivatives of methane, respectively, and R is the molar gas constant.

The values of D_i and σ_i for all the halogen derivatives of methane are given in Appendix 8.

Calculations according to equations (a)-(d) are possible if the standard entropies for the corresponding reactants are known.

Example 86. Calculate S°_{298} for gaseous CH_2BrI according to the known values of this quantity 69.84 and 73.97 cal/mol·K for the methane derivatives CH_2Br_2 and CH_2I_2 [49] if the molecular weights M, products of the principal moments of inertia $D = I_A I_B I_C$, and the symmetry numbers σ equal 112.942, 173.858, and 267.866; 3.11 × × 10^{-113}, 1.41 × 10^{-113}, and 5.69 × 10^{-113} g³·cm⁶; and 1, 2, and 2, respectively (Appendix 8).

Solution. We calculate S°_{298} according to Eq. (1.48):

$$Y_i = \frac{1}{n} \sum_i \delta_j Y_j - \Delta M - \Delta D + \Delta \sigma$$

We find the first addend in Eq. (1.46) with the aid of Eq. (1.47):

$$\frac{1}{n} \sum_j \delta_j Y_j = \frac{1}{2} (S^\circ_{CH_2Br_2} + S^\circ_{CH_2I_2}) = 0.5 (69.84 + 73.97) =$$

$$= 71.905 \text{ e.u.}$$

We calculate ΔM using Eq. (1.49):

$$\Delta M = \frac{3R}{2 \times 2} [(\ln M_{CH_2Br_2} + \ln M_{CH_2I_2}) - 2 \ln M_{CH_2BrI}]$$

$$\Delta M = \frac{3 \times 1.987 \times 2.3}{4} [(\log 173.86 + \log 267.87) - 2 \log 112.94] =$$

$$= -0.069 \text{ e.u.}$$

We find ΔD according to Eq. (1.50):

$$\Delta D = \frac{R}{2 \times 2} [(\ln D_{CH_2Br_2} + \ln D_{CH_2I_2}) - 2 \ln D_{CH_2BrI}]$$

$$\Delta D = \frac{1.987 \times 2.3}{4} [(\log 1.41 \times 10^{-113} + \log 5.69 \times 10^{-113}) -$$

$$- 2 \log 3.11 \times 10^{-113}] = -0.093 \text{ e.u.}$$

Finally, we determine $\Delta \sigma$ by Eq. (1.51):

$$\Delta \sigma = \frac{R}{n} [(\ln \sigma_{CH_2Br_2} + \ln \sigma_{CH_2I_2}) - n \ln \sigma_{CH_2BrI}]$$

$$\Delta \sigma = \frac{1.987 \times 2.3}{2} [(\log 2 + \log 2) - 2 \log 1] = 1.377 \text{ e.u.}$$

Thus, for gaseous CH_2BrI, we have

$$S^\circ_{298} = 71.905 + 0.069 + 0.093 + 1.377 = 73.44 \text{ cal/mol} \cdot K$$

This quantity agrees quite well with the value 73.49 found from spectral data in [60].

Example 87. Calculate the standard entropy of crystalline alumin ium oxide. Use the empirical equation (2.34).

Solution. The molecular weight of aluminium oxide $M = 101.96$. In Appendix 14, we find $A = 33.1$ and $B = -54.4$. Hence by Eq. (2.34), we have

$$(S^\circ_{298})^c = A \log M + B = 33.1 \log 101.96 - 54.4 = 12.10 \text{ cal/mol} \cdot K$$

The tabulated value is 12.18 cal/mol$\cdot$K [20].

Example 88. Use Eq. (2.35) to calculate $(S^\circ_{298})^g$ for water. Compare the result with the tabulated value equal to 45.11 cal/mol$\cdot$K [20].

Solution. For the triatomic molecule of water, the constants of Eq. (2.35) according to Appendix 15 are $A = 0.211$ and $\log B = 1.386$. The molecular weight of H_2O is $M = 18$. Therefore by Eq. (2.35), we have

$$\log S^\circ_{298} = A \log M + \log B = 0.211 \log 18 + 1.386 =$$
$$= 0.211 \times 1.2553 + 1.386 = 1.640$$

whence

$$(S^\circ_{298})^g = 43.7 \text{ cal/mol} \cdot K$$

The relative error is about 3.22%.

2.5
Calculation of the Change in Entropy as a Result of a Reaction

To calculate the equilibrium constant of a reaction, we must know the change in entropy ΔS as a result of the reaction. We shall consider a reaction following the scheme

$$\nu_1 A_1 + \nu_2 A_2 + \ldots \rightleftarrows \nu'_1 A'_1 + \nu'_2 A'_2 + \ldots \qquad (2.37)$$

where A_i and A'_i = symbols of the reactants and products, respectively

ν_i and ν'_i = stoichiometric coefficients of the reactants and products, respectively.

If we know the absolute values of the entropies of the reactants and products, then the change in entropy as a result of a reaction

will be

$$\Delta S = (v_1' S_{A_1'} + v_2' S_{A_2'} + \ldots) - (v_1 S_{A_1} + v_2 S_{A_2} + \ldots) \qquad (2.38)$$

The absolute values of the entropy of reagents needed for calculations are found in tables of standard thermodynamic quantities or are calculated by one of the methods considered above.

Example 89. Calculate the change in entropy as a result of the reaction of incomplete oxidation of methane

$$CH_4 + \frac{3}{4} O_2 = \frac{1}{6} C_6H_6(g) + \frac{3}{2} H_2O(g)$$
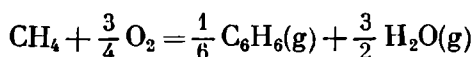
conducted in standard conditions at 25 °C.

Solution. We find the standard entropies at 25 °C with the aid of tables for the reagents:

$$CH_4 + \frac{3}{4} O_2 = \frac{1}{6} C_6H_6 + \frac{3}{2} H_2O$$
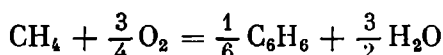
$(S_{298}^\circ)^g$, cal/mol·K   44.50   49.00   64.34   45.11

In accordance with Eq. (2.38), the change in entropy will be

$$\Delta S_{298}^\circ = \left(\frac{1}{6} \times 64.34 + \frac{3}{2} \times 45.11 \right) - \left(44.50 + \frac{3}{4} \times 49.00 \right) =$$

$$= 78.30 - 81.25 = -2.95 \text{ cal/K}$$

Example 90. Determine the change in entropy as a result of the reaction of alkylation of benzene with isobutylene with the formation of isobutylbenzene conducted in standard conditions at 25 °C in the gaseous phase.

Solution. We write the equation of the reaction and find the values of S_{298}° of the reagents in the relevant tables (Appendix 1):

$$C_6H_6(g) + C_4H_8(g) = C_6H_5 - C_4H_9(g)$$
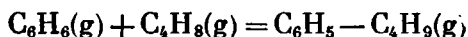
$(S_{298}^\circ)^g$, cal/mol·K   64.34   70.17   95.20

(The value 95.20 has been obtained by calculations given below.)

The value of $(S_{298}^\circ)^g$ for isobutylbenzene is not given in tables of standard quantities. We therefore find it by one of the empirical methods considered above, for example by the method of introducing corrections for the substitution of hydrogen by $-CH_3$ and other

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groups (see the tables in Appendix 7):

$$C_6H_6 \xrightarrow[\Delta S = 12.08]{} C_6H_5 - CH_3 \xrightarrow[\Delta S = 10.76]{(A)=1, (B)=5}$$

$$S^\circ_{298} = 64.34$$

$$\rightarrow C_6H_5 - CH_2 - CH_3 \xrightarrow[\Delta S = 6.72]{(A)=2, (B)=5}$$

$$\rightarrow \underset{\underset{CH_3}{\overset{\displaystyle |}{}}}{\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{}}}{C_6H_5 - CH}} \xrightarrow[\Delta S = 1.30]{(A)=3, (B)=5} \underset{\underset{CH_3}{\overset{\displaystyle |}{}}}{\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{}}}{C_6H_5 - C - CH_3}}$$
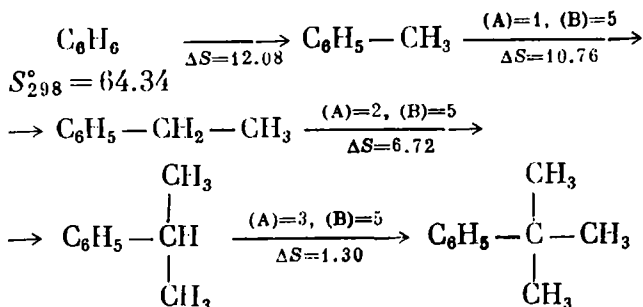
Hence,

$$(S^\circ_{298})^g = 64.34 + 12.08 + 10.76 + 6.72 + 1.30 = 95.20 \text{ cal/mol} \cdot K$$

According to Eq. (2.38), the change in entropy as a result of the reaction will be

$$\Delta S^\circ_{298} = 95.20 - 64.34 - 70.17 = -39.31 \text{ cal/K}$$

Problems

117. Find the change in entropy for the hundred-fold isothermal expansion of one mole of an ideal gas.

118. One mole of ammonia at 25 °C and 1 atm is heated with the pressure kept constant until its volume increases three-fold (ammonia expands like an ideal gas). Determine the change in entropy.

119. One mole of an ideal gas occupying a volume of 20 dm³ is subjected to isothermal expansion. What final volume does a change in entropy of 9.15 cal/mol·K correspond to?

120. By how much will the entropy change as a result of an isothermal change of state of 10 g of krypton if $V_1 = 50$ dm³, $p_1 = 1$ atm, $V_2 = 200$ dm³, and $p_2 = 0.25$ atm?

121. 11.2 dm³ of nitrogen are heated from 0 to 50 °C, and the pressure is simultaneously reduced from 1 to 0.01 atm. Find the change in entropy if nitrogen is assumed to be an ideal gas and $C_p = 7.0$ cal/mol·K.

122. Find the change in entropy in the isothermal ($t = 80$ °C) compression of benzene vapour from a pressure of 0.4 to 1 atm with the following condensation and cooling of the liquid benzene to 60 °C if the molar heat of vaporization of benzene at 80 °C is 7380 cal/mol and $C_p^{lq} = 0.43$ cal/g·K. Assume that the benzene vapour is an ideal gas.

123. What is the change in entropy when one mole of nitrogen in standard conditions at 25 °C passes over to a temperature of 200 °C and a volume of 50 dm³? Given that $C_p = 7R/2$.

124. Considering C_p for carbon dioxide to equal $7R/2$ and assuming that CO_2 is an ideal gas, calculate the change in entropy of 0.5 mole of this gas when it passes over from standard conditions at 25 °C to a temperature of 100 °C and a pressure of 3 atm.

125. The true molar heat capacity of CO is expressed by the equation

$$C_p = 6.342 + 1.836 \times 10^{-3}T \text{ cal/mol·K}$$

One mole of CO taken at 0 °C expands isobarically. What will the final temperature be if as a result of expansion the entropy grows by two units?

126. Find the change in entropy of 1 kg of air when heated from −50 to +50 °C. The pressure changes from 10 bars to 1 bar. The specific heat capacity of air is 1.005 J/g·K. The average molecular weight of air is 29.

127. Find the change in entropy when three moles of O_2 pass over from a volume of 33.6 dm³ under a pressure of 2 atm to a volume of 67.2 dm³ under a pressure of 1 atm. Assume that $C_p = 29.371$ J/mol·K.

128. How many times must the volume of one mole of an ideal gas be increased for its entropy to grow by 1 kcal/kg·K?

129. Calculate the entropies of methane and hydrogen at 600 °C if at 25 °C their entropies are 43.4 and 31.23 cal/mol·K. respectively; heating from 25 to 600 °C proceeds at constant volume. Assume that the gases are (a) real; and (b) ideal.

130. According to the Gibbs theorem, the entropy of a mixture of two ideal gases occupying the volume V equals the sum of the entropies of the two gases taken separately, calculated on the assumption that each of them occupies the entire volume V. Prove that this theorem cannot be applied to identical gases. Explain Gibbs' paradox.

131. 30 dm³ of carbon dioxide diffuse into 30 dm³ of oxygen at a constant total pressure of 2 atm and a temperature of 0 °C. Calculate the growth in entropy.

132. Show that in the isothermal mixing of ideal gases under the pressure p, the entropy changes (calculated per mole of the mixture) by $-R \sum x_i \ln x_i$, where x_i is the mole fraction of the i-th component of the mixture.

133. Use the data in the following table to find the growth in entropy when V_A m³ of gas A under a pressure of 1.013×10^5 N/m² and at a temperature of T_A K are mixed with V_B m³ of gas B under a pressure of p_B (N/m²) and at a temperature of T_B K. Assume that

both gases obey the laws of ideal gases and that mixing occurs in a vessel with a constant volume.

Calcula-tion No.	$V_A \times 10^4$, m³	A	T_A, K	$V_B \times 10^4$, m³	B	T_B, K	p_B, N/m²
1	1	H_2	303	2	N_2	290	101 325
2	5	H_2O	388	6	O_2	310	101 305
3	7	He	275	8	CO_2	290	131 722
4	1	He	277	5	H_2	303	303 975
5	7	CH_4	268	9	C_2H_6	288	172 252
6	2	CH_4	298	3	3Ne	283	303 975
7	3.3	CO	268	4	C_2H_6	300	709 270
8	6	CO_2	280	7	N_2	310	141.855
9	7	CO_2	258	9	CO	278	40 530
10	2	CO_2	303	4	CH_4	289	810 060
11	3	C_2H_6	268	6	Xe	296	206 450
12	8	C_2H_6	313	9	CH_4	289	151 987
13	7	N_2	290	9	Cl_2	299	192 517
14	4	N_2	293	7	H_2O	383	101 325
15	6	O_2	333	8	He	297	506 625
16	1	O_2	333	4	N_2	290	101 325
17	1	O_2	303	3	H_2	298	101 325
18	4	F_2	281	5	Ar	292	182 385
19	1	Ne	278	8	Cl_2	296	50 662
20	5	Cl_2	243	7	Cl_2	278	50 662
21	1	Cl_2	308	7	Ar	292	253 312
22	1	Ar	276	6	He	291	151 987
23	2	Kr	276	6	CO_2	208	121 590
24	2	Kr	278	7	CO	308	40 530
25	3	Xe	263	6	F_2	286	172 252

1134. The molar heat of vaporization ΔH_{vap} is spent when a substance whose vapour obeys the ideal gas laws passes over from the liquid to the gaseous state at a temperature of t °C and a pressure of 1 atm. Calculate (1) the change in entropy as a result of vaporization of one mole of substance A in the given conditions; (2) the change in entropy if the vapour of one mole of substance A is heated from t to $(t + 15)$ °C (a) at constant volume, and (b) at constant pressure; and (3) by how many kelvins would the temperature of the substance grow if the change in internal energy upon the transition from the liquid to the gaseous state were expressed in elevation of the temperature? Take the data needed for the calculations from reference books. The values of t and A are given in the following table.

Calculation No.	t, °C	A	Calculation No.	t, °C	A
1	−253	H_2	8	−33.5	NH_3
2	10	H_2O	9	−152	NO
3	20	C_6H_6	10	−188	O_2
4	−84	HCl	11	−11	SO_2
5	50	CO	12	−22	Cl_2
6	0	CO_2	13	58	Br_2
7	−200	N_2	14	−161.6	CH_4

135. Show that the entropy of one mole of an ideal gas and of a gas obeying the van der Waals equation are related by the equation

$$S = S_{id} - \frac{Rb}{V}$$

136. One mole of water vapour is condensed at 100 °C, the water is cooled to 0 °C and freezes at this temperature. Find the change in entropy if the heat of vaporization at the boiling point and the heat of fusion at the freezing point are 539.7 and 79.7 cal/g, respectively, and the mean specific heat capacity of liquid water is 1 cal/g·K.

137. Find the change in entropy in the process of condensation of supercooled water vapour if $t = 25$ °C and $p = 1$ atm. Assume that water vapour is an ideal gas.

138. What is the change in entropy in the distillation of one mole of cyclohexane if its molar heat of fusion at 280 K is 628 cal/mol, and its molar heat of vaporization is 7983 cal/mol? Perform the calculations for the mean temperature.

139. Bromobenzene boils at 429.8 K. Its specific heat of vaporization at this temperature is 241.9 × 10³ J/kg (57.8 cal/g). Find the change in entropy upon the vaporization of 10 kg of bromobenzene expressing the entropy in J/mol·K and cal/mol·K.

140. Calculate the change in entropy in heating 16 kg of O_2 from 273 to 373 K (a) at $V = $ const; and (b) at $p = $ const.

141. Find the change in entropy in heating (cooling) m kg of substance A from the temperature T_1 to T_2 at constant pressure if its melting and boiling points, heat capacity in the solid, liquid, and gaseous state, and its heats of fusion and vaporization are known (see reference books, for example [8]). The values of A, m, T_1, and T_2 are given in the following table.

Calcula- tion No.	A	m	T_1	T_2
1	Br_2	25	373	173
2	H_2O	45	421	223
3	Hg	40	193	673
4	CCl_4	80	323	373
5	Formic acid H·COOH	10	393	273
6	CH_3OH	15	160	350
7	Trichloroacetic acid CCl_3·COOH	80	303	473
8	Acetic acid	8	423	223
9	Ethanol	50	373	143
10	Acetone	10	173	373
11	Ethyl ether	50	143	323
12	n-Pentane	35	323	133
13	Benzene	1	383	273
14	Cyclohexane	100	373	273
15	n-Hexane	10	173	373
16	Toluene	50	423	173
17	Naphthalene	25	328	523
18	o-Xylene	60	423	223
19	n-Xylene	40	523	303
20	m-Xylene	75	579	323

142. Calculate the change in entropy upon heating one mole of carbon dioxide from 0 to 900 °C under atmospheric pressure. The heat capacity depending on the temperature is determined by the equation

$$C_p = 10.34 + 2.74 \times 10^{-3}T - 1.955 \times 10^5 T^{-2} \text{ cal/mol·K}$$

143. The temperature dependence of the density of antimony trichloride within the interval from 75 to 150 °C is expressed by the equation

$$\rho = 2.8131 - 1.636 \times 10^{-3}t - 3.2 \times 10^{-6}t^2 \text{ g/cm}^3$$

Find the change in entropy of one mole of $SbCl_3$ when the pressure changes by 1 atm and at 100 °C.

144. Show that if the change in the heat capacity C_p with the temperature T is given by the equation

$$C_p = a + bT + \frac{c'}{T^2}$$

then the temperature dependence of the entropy within the temperature interval from T_1 and T_2 is expressed by the equation

$$S_{T_2} - S_{T_1} = a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c'}{2} \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right)$$

145. Considering carbon monoxide to be an ideal gas, find its molar entropy at 20 °C and 50 atm if its entropy at 25 °C and 1 atm equals 47.32 cal/mol·K, and $C_p = 6.60 + 1.20 \times 10^{-3} T$.

146. What does the change in the entropy equal in the process of separation of an ideal gas mixture into its components provided that the pressure and temperature are constant?

147. Find the growth in the entropy of propane per unit of volume at −47.75 °C if the pressure dependence of the boiling point is expressed by the equation

$$\log p = 6.856\,58 - \frac{798.456}{248.581 + t} \quad \text{mm Hg}$$

148. Find the change in entropy in heating one mole of cobaltous chloride by one kelvin at $p = $ const and 470 °C if its true molar heat capacity is expressed by the equation

$$C_p = 14.41 + 14.60 \times 10^{-3} T$$

149. The molar heat capacity of gaseous methane is expressed by the equation

$$C_p = 4.171 + 14.45 \times 10^{-3} T \quad \text{cal/mol·K}$$

The standard entropy of methane $S_{298}^\circ = 44.50$ cal/mol·K. Determine the entropy of 1×10^{-3} m^3 of methane at 800 K and 1 atm.

150. The molar heat capacity of CO is expressed by the equation

$$C_p = 6.342 + 1.836 \times 10^{-3} T$$

Calculate the molar entropy of CO at 596 K and 2 atm if the standard entropy $S_{298}^\circ = 47.301$ cal/mol·K.

151. The specific heat capacity of silicon at 0 °C is $C_p = 0.162$ cal/g·K. Determine the change in entropy per kelvin at $p = $ const.

152. The growth in the boiling point of quinoline when the pressure changes by 1 atm is 0.058 824 (at the boiling point). Calculate the growth in entropy per unit of volume at this temperature.

153. Using the data given below, compute the absolute values of the entropy at $T = 298.15$ K, S_{298}^g, for the following gaseous substances [3]:

(a) oxygen O_2

T	c_p	T	c_p	T	c_p
15	1.7	45	11.0	90	13.5
20	3.6	50	11.0	90.13****	1628.8****
20.56*	22.42*	54.39***	106.3***	200	6.96
30	6.6	60	13.2	300	7.02
40	9.8	70.3	13.3	400	7.20
43.76**	177.6**	80	13.4	500	7.43

$*T_{tr}^{I}, \Delta H_{tr}^{I}; \ **T_{tr}^{II}, \Delta H_{tr}^{II}; \ ***T_{m}, \Delta H_{f}; \ ****T_{b}, \Delta H_{vap}.$

(b) ammonia NH_3

T	c_p	T	c_p	T	c_p
15	0.2	175	10.7	243	8.22
25	0.8	195.36*	1351.6*	253	8.27
50	2.7	200	12.5	263	8.32
75	4.4	225	12.9	273	8.37
100	6.2	235	13.1	283	8.43
125	7.8	239.68**	5581**	293	8.49
150	9.2			303	8.55

$*T_{m}, \Delta H_{f}; \ **T_{b}, \Delta H_{vap}.$

(c) neopentane C_5H_{12}

T	c_p	T	c_p	T	c_p
15	2.08	140.02*	615.9*	260	36.22
20	3.97	160	25.50	270	37.38
40	8.70	180	26.82	280	39.44
60	11.52	200	28.02	282.6***	5438***
80	14.36	220	29.48	300	29.1
100	17.82	240	32.59	344	29.8
120	21.63	256.6**	778.2**		

$*T_{tr}, \Delta H_{tr}; \ **T_{m}, \Delta H_{f}; \ ***T_{b}, \Delta H_{vap}.$

Here T_{tr}, T_m, and T_b are the points of transformation in the solid phase, of melting, and of boiling, respectively; and ΔH_{tr}, ΔH_f, and ΔH_{vap} are the molar heats of transformation in the solid phase, of fusion, and of vaporization, respectively.

The temperature in the tables is expressed in K, the true molar heat capacity at $p = $ const, C_p, in cal/mol·K, and the heats of phase transitions ΔH in cal/mol.

154. Using the data given below, calculate the absolute entropy of the liquid hydrocarbons indicated at $T = 298.15$ K [3]:

(a) *n*-hexane C_6H_{14}

T	c_p	T	c_p	T	c_p
90	17.55	180	40.40	300	45.17
100	18.90	200	41.01	320	48.54
120	21.96	220	42.80	341.3**	7100**
140	25.07	240	46.06	350	35.58
160	29.00	260	48.77	400	43.43
178.6*	3000*	280	46.78	450	45.06

*T_m, ΔH_f; **T_b, ΔH_{vap}.

(b) 2,2,4-trimethylpentane C_8H_{18}

T	c_p	T.	c_p	T	c_p
14.4	1.97	160.7	35.92	301.9	57.60
22.1	4.87	165.8*	2201.6*	317.3	59.40
40.2	10.44	171.2	44.58	372.3**	7410**
60.8	14.94	182.9	45.43	423	61.6
81.8	19.24	203.8	47.15	442	63.8
100.7	23.37	233.4	50.06	448	65.6
119.5	27.42	256.6	52.50	458	66.7
141.9	31.91	280.0	54.97		

*T_m, ΔH_f; **T_b, ΔH_{vap}.

(c) toluene $C_6H_5 \cdot CH_3$

T	c_p	T	c_p	T	c_p
20	3.15	140	17.74	260	34.24
40	8.34	160	19.09	280	36.11
60	11.66	178.2*	1560*	383.5**	8090**
80	13.55	200	32.52	393	33.00
100	14.79	220	33.22	428	36.01
120	16.36	240	33.71	463	38.30

$*T_m, \Delta H_f; **T_b, \Delta H_{vap}.$

The same units and symbols are used as in Problem 153.
155. Calculate S°_{500} for the following vapours:
(a) benzene C_6H_6

T	c_p	T	c_p	T	c_p
10	0.35	200	20.16	320	33.58
20	1.84	240	24.77	352.8**	7390**
40	6.47	260	27.76	388	26.3
60	9.32	270	29.35	417	28.4
80	10.85	278.6*	2350*	428	28.6
120	13.28	280	31.02	463	30.5
160	16.30	300	32.27	481	31.6

$*T_m, \Delta H_f; **T_b, \Delta H_{vap}.$

(b) m-xylene $C_6H_4(CH_3)_2$

T	c_p	T	c_p	T	c_p
15	1.74	140	21.03	260	40.78
20	3.28	160	22.96	280	42.53
40	9.86	180	25.06	300	43.93
60	13.25	200	27.15	412.2**	8740**
80	15.54	220	29.22	393	39.20
100	17.41	225.3*	2765*	428	42.70
120	19.15	240	39.71	463	45.70

$*T_m, \Delta H_f; **T_b, \Delta H_{vap}.$

The same units and symbols are used as in Problem 153.

156. Using the following data, calculate the molar entropy of gaseous isobutylene at 298.15 K: $S_{90} = 10.81$ cal/mol·K, $T_m = 147.46$ K, $\Delta H_f = 25.22$ cal/g, $T_b = 291.06$ K, $\Delta H_{vap} = 96.5$ cal/g, $\overline{C}_p^g$ within the interval from 226 to 298 K equals 20 cal/mol·K, and the true heat capacity depends on the temperature as follows:

T, K . . .	93.3	105.5	118.9	139.2	166.1	179.8	210.2	253.1
C_p, cal/g·K	0.2498	0.2749	0.3056	0.4547	0.4621	0.4681	0.4860	0.5173

157. The entropy of liquid *o*-xylene $S_{298}^{lq} = 58.8$ cal/mol·K, and its saturated vapour pressure within the temperature interval from 0 to 60 °C is given by the equation

$$\log p = \frac{-3327.16}{T} - 8.0 \log T + 31.7771$$

Calculate the standard entropy at 25 °C of gaseous *o*-xylene.

158. Using the data of Problem 153, calculate the standard entropies of gaseous oxygen, ammonia, and 2,2-dimethylpropane at 25 °C if their critical parameters are as follows:

Substance	O_2	NH_3	C_5H_{12}
T_{cr}, K	154.8	405.5	433.8
p_{cr}, atm	49.7	111.3	31.6

Compare the results obtained with $(S_{298}^\circ)^g$ equal to 49.0, 46.0, and 73.2 cal/mol·K given in [20].

159. Having determined the absolute values of the entropy S_{298}^{lq} at 298.15 K for liquid *n*-hexane C_6H_{14}, 2,2,4-trimethylpentane C_8H_{18}, benzene C_6H_6, toluene $C_6H_5 \cdot CH_3$, and *m*-xylene $C_6H_4(CH_3)_2$ with the aid of the initial data of problems 154 and 155, calculate their standard entropies $(S_{298}^\circ)^g$ in the gaseous state at $T = 298.15$ K. Find the saturated vapour pressure for each of the hydrocarbons listed above with the aid of the equation

$$\log p = A - \frac{B}{t + C} \text{ mm Hg}$$

The coefficients A, B, and C and the critical parameters have the following values:

Hydrocarbon	Temperature interval, °C from	to	A	B	C	T_{cr}, K	p_{cr}, atm
n-C_6H_{14}	—60	110	6.877 76	1171.53	224.37	507.9	29.5
C_8H_{18}	20	150	6.825 46	1294.88	218.42	544.3	25.5
C_6H_6	5.5	160	6.912 10	1214.64	221.60	561.7	47.8
$C_6H_5 \cdot CH_3$	20	200	6.953 34	1343.94	219.38	593.8	41.6
m-$C_6H_4(CH_3)_2$	25	45	7.368 10	1658.23	232.30	619.2	35.0

160. Using the empirical method of introducing corrections for the substitution of hydrogen by $-CH_3$ and other groups, calculate $(S^\circ_{298})^g$ for the following substances: (a) formaldehyde CHOH; (b) ethylene oxide $(CH_2)_2O$; (c) ethylene glycol $CH_2OH \cdot CH_2OH$; (d) isopropyl alcohol C_3H_7OH; (e) $n\text{-}C_5H_{11}OH$; (f) dichloromethane CH_2Cl_2; (g) tetrachloromethane CCl_4; (h) phenyltrifluoromethane $C_6H_5CF_3$; (i) dimethylamine $(CH_3)_2NH$; (j) aniline $C_6H_5NH_2$; (k) 2,2-dimethylpropane C_5H_{12}; and (l) m-xylene $C_6H_4(CH_3)_2$. Compare the results with the tabulated values of $(S^\circ_{298})^g$ [20]: (a) 52.29; (b) 58.25; (c) 77.33; (d) 73.2; (e) 60.9; (f) 64.6; (g) 74.0; (h) 89.1; (i) 65.27; (j) 71.9; (k) 73.23; and (l) 85.37 cal/mol·K.

161. Use Eq. (2.29) to determine $(S^\circ_{298})^g$ for the following normal hydrocarbons: (a) pentane C_5H_{12}; (b) nonane C_9H_{20}; (c) eicosane $C_{20}H_{42}$; and (d) dodecane $C_{12}H_{26}$. Compare the results of the calculations with the tabulated values of $(S^\circ_{298})^g$ [20]: (a) 83.13; (b) 122.1; (c) 223.2; and (d) 149.8 cal/mol·K.

162. Use Eq. (2.30) to calculate $(S^\circ_{298})^{lq}$ for the following hydrocarbons: (a) n-octane; (b) 2,2,4-trimethylpentane; (c) n-nonane; (d) n-butylbenzene; (e) ethylbenzene; and (f) methylcyclohexane. Compare the results with the tabulated values of $(S^\circ_{298})^{lq}$ [20]: (a) 86.6; (b) 81.1; (c) 94.3; (d) 79.8; (e) 64.4; and (f) 63.7 cal/mol·K.

163. Use Eq. (2.33) to assess $(S^\circ_{298})^{lq}$ for the following hydrocarbons: (a) aniline $C_6H_5NH_2$; (b) 1,4-dioxane $(CH_2)_4O_2$; and (c) glycine $CH_2NH_2 \cdot COOH$ if their true molar heat capacities $(C^\circ_p)^{lq}$ equal 4.7, 36.5, and 23.7 cal/mol·K, respectively. Compare the results with the tabulated values of $(S^\circ_{298})^{lq}$ [20]: (a) 45.8; (b) 47.0; and (c) 26.0 cal/mol·K.

164. Determine $(S^\circ_{298})^c$ for the following substances: (a) MgO; (b) BaO; (c) ZnO; (d) K_2O; (e) Na_2O; (f) Cu_2O; (g) Sb_2O_3; (h) Bi_2O_3; (i) As_2O_3; (j) Sb_2O_5; (k) P_2O_5; and (l) As_2O_5. Use Eq. (2.34).

165. Calculate $(S^\circ_{298})^g$ for the following substances: (a) H_2; (b) Cl_2O; (c) NH_3; (d) SiF_4; and (e) N_2O_4. Use Eq. (2.36). Compare the results with the values of $(S^\circ_{298})^g$ given in [20]: (a) 31.21; (b) 63.64; (c) 46.01; (d) 67.3; and (e) 72.73 cal/mol·K.

166. Using tables of standard quantities (Appendix 1), calculate ΔS°_{298} for the following reactions:

(a) $H_2 + \dfrac{1}{2} O_2 = H_2O(lq)$

(b) $H_2 + Cl_2 = 2HCl(g)$

(c) $C_3H_8(g) + C_2H_6(g) = n\text{-}C_5H_{12}(g) + H_2$

(d) $CH_4 + \dfrac{1}{2} O_2 = CH_3OH(g)$

(e) $C + CO_2 = 2CO$

(f) $MgO + H_2 = Mg + H_2O(lq)$
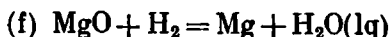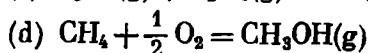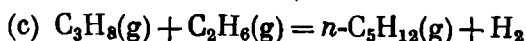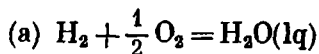
167. Find the temperature dependence of $\Delta S°$ for the reaction

$$2C_2H_5OH \text{ (g)} \rightarrow C_4H_6 \text{ (1,3-butadiene)} + 2H_2O(g) + H_2$$
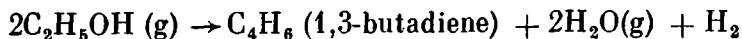
Use Appendix 1.

168. Using Appendix 1, determine the change in entropy as a result of the reaction

$$2H_2 + O_2 = 2H_2O$$
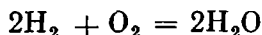
conducted in the gaseous phase at 500 K in standard conditions.

169. Find the equation of the temperature dependence of the change in entropy as a result of the reaction of hydrogenation of benzene conducted in the gaseous phase in standard conditions. Use Appendix 1.

170. Using Maslovs' method, determine $(S_{298}^°)^g$ for CHFClBr if the values of $S_{298}^°$ for CF_3Cl, CF_3Br, and CF_3H equal 68.23, 71.09, and 62.04 cal/mol·K, respectively [49]. Take the values of D and σ needed for the calculations from Appendix 8. Compare the result with $S_{298}^° = 72.88$ cal/mol·K obtained from spectral data [60].

171. Find $S_{298}^°$ for gaseous CF_3H if the values of $S_{298}^°$, D, and σ for CF_4 and CF_2H_2 equal 62.457 and 58.94 cal/mol·K [20], 3.24 × × 10^3 and 1.17 × 10^2 $g^3 \cdot cm^3$ × 10^{-117}, and 12 and 2 (Appendix 8), respectively. Compare the found value with 62.21 cal/mol·K [20].

172. Use Appendix 8 to find the standard entropy at 25 °C of gaseous CF_2Cl_2 if the values of $S_{298}^°$ for CF_4 and CCl_4 are known and equal 62.457 and 74.03 cal/mol·K, respectively [20]. Compare the result with $S_{298}^° = 71.84$ cal/mol·K calculated from spectral data.

3

Methods for Calculating the Changes in the Gibbs Energy ΔG_T in the Course of a Reaction

3.1
Basic Methods of Calculation

The thermodynamic possibility of the spontaneous proceeding of a chemical reaction is determined by the sign and the absolute value of the change in the Gibbs energy ΔG_T or the Helmholtz energy ΔA_T in the course of the reaction (i.e. the change in the isobaric-isothermal or isochoric-isothermal potential) found for a constant temperature. For any reaction of the kind

$$\nu_1 A_1 + \nu_2 A_2 + \ldots \rightleftarrows \nu_1' A_1' + \nu_2' A_2' + \ldots$$
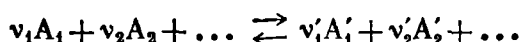
conducted isothermally and isobarically, ΔG_T is determined according to the equation of a reaction isotherm

$$\Delta G_T = RT \left\{ \ln \frac{a_{A_1'}^{\nu_1'} a_{A_2'}^{\nu_2'} \ldots}{a_{A_1}^{\nu_1} a_{A_2}^{\nu_2} \ldots} - \ln K_a \right\} \tag{3.1}$$

where ν_i = stoichiometric coefficient of the i-th reactant (and ν_i' that of the i-th product)

a_{A_i} = activity of the i-th reactant at any moment during the reaction until equilibrium is reached (generally the activity in the initial state of the system)

K_a = equilibrium constant of the reaction at the given temperature (it is determined from the law of mass action, in which the equilibrium concentrations of the reagents are expressed through the activities).

If the reagents are gaseous, then $a_{A_i} = f_{A_i}$ and $K_a = K_f$ (where the equilibrium concentrations of the reagents are expressed through the partial fugacities). For systems described by an equation of state for an ideal gas, i.e. systems in which the forces of interaction between the molecules may be disregarded, we have $f_{A_i} = p_{A_i}$ (the partial pressures) and $K_f = K_p$.

Equation (3.1) permits us to calculate ΔG_T for a reaction if we know its equilibrium constant (in any of the forms indicated above) and the concentrations of the reagents in the initial state of the system. When $\Delta G_T < 0$, a reaction proceeds spontaneously in the forward direction (from left to right) until equilibrium sets in in the system, and the greater the absolute value of ΔG_T, the greater is the possibility of the given reaction proceeding spontaneously. When $\Delta G_T > 0$, the reaction proceeds spontaneously in the reverse direction, from right to left. For greater detail see Chap. 14 in [18].

Example 91. It has been found experimentally that the dehydrogenation of methyl alcohol results in the formation of methyl formate

$$2CH_3OH(g) \rightleftarrows HCOOCH_3(g) + 2H_2$$

The equilibrium constant of the given reaction at 504 K is 0.140 [9]. In what direction will the reaction proceed at this temperature if the initial mixture has the following composition (in mole %): 82% of alcohol, 10% of hydrogen, and the remainder the ester? The total pressure in the system is 1.2 atm.

Solution. The partial pressures of the reagents (in atm) are

$$p_{CH_3OH} = 1.2 \times 0.82 = 0.984; \quad p_{H_2} = 1.2 \times 0.10 = 0.12;$$

and $\quad p_{HCOOCH_3} = 1.2 \times 0.08 = 0.096$

We calculate ΔG_T by Eq. (3.1):

$$\Delta G_T = 1.987 \times 2.3 \times 504 \left(\log \frac{0.12^2 \times 0.096}{0.984^2} - \log 0.14 \right) =$$
$$= -4580 \text{ cal}$$

$\Delta G_T < 0$, hence the reaction will proceed spontaneously in the forward direction.

To compare ΔG_T for different reactions, we must have identical initial states of a system. It was agreed to choose such a state as the initial one, called standard, when the activity of each reactant and each product of a reaction corresponds to unit molality. If the reagents are gaseous, the partial fugacities of all the reagents in the initial state must equal unity $(f_{A_1} = f_{A_2} = \ldots = f_{A_1'} = f_{A_2'} = \ldots$ $\ldots = 1$ atm); for ideal gaseous systems the partial pressures of all the reagents equal 1 atm. The system may be at any temperature, but upon transition from the initial state to the equilibrium one the temperature must be constant. Hence,

$$\Delta G_T^\circ = -RT \ln K_a \tag{3.2}$$

and for an ideal gaseous system

$$\Delta G_T^\circ = -RT \ln K_p \tag{3.3}$$

Example 92. Studying of the reaction

$$CH_2 = \underset{\underset{CH_3}{\mid}}{C} - CH_3(g) + HCl(g) \;\rightarrow\; CH_3 - \underset{\underset{CH_3}{\mid}}{CCl} - CH_3(g)$$
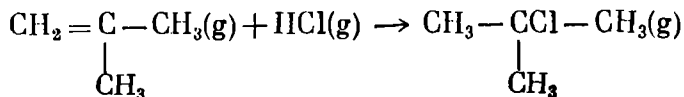
made it possible to determine that at 421 K we have $K_p = 10.6\ \text{atm}^{-1}$ [9]. Calculate ΔG°_{421} for the reaction.

Solution. By Eq. (3.3)

$$\Delta G^\circ_{421} = -4.576 \times 421 \log 10.6 = -1970\ \text{cal}$$

For reactions in galvanic cells, ΔG_T can be determined according to experimental data by the equation

$$-\Delta G_T = nFE \tag{3.4}$$

where n = valence of the ions

F = Faraday constant

E = maximum potential difference measured in an open circuit provided that the right-hand electrode is charged positively.

Thus, for the circuit

$$\overset{-}{Me_1} \mid Me_1^+(a_1) \parallel Me_2^+(a_2) \overset{+}{\mid} Me_2$$
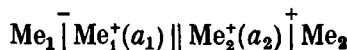
$$E = \varepsilon_2 - \varepsilon_1 = \varepsilon_2^\circ - \varepsilon_1^\bullet + \frac{RT}{nF} \log \frac{a_{2Me_2^+}}{a_{1Me_1^+}} \tag{3.5}$$

Example 93. A galvanic cell is formed of cobalt and copper immersed in solutions of their chlorides ($n = 2$). Find ΔG for the reaction in the cell at 298 K if the molalities of $CoCl_2$ and $CuCl_2$ are $m = 1$ and $m = 0.05$, respectively.

Solution.

$$Co \mid CoCl_2 \parallel CuCl_2 \mid Cu$$
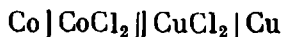
$$\varepsilon_1\ a_{Co^{2+}}\quad a_{Cu^{2+}}\ \varepsilon_2$$

We find the standard electrode potentials in [8]: $\varepsilon^\circ = 0.337$ V for Cu/Cu^{2+} and $\varepsilon^\circ = -0.277$ V for Co/Co^{2+}. The activity coefficients are [8]: $\gamma_\pm = 0.577$ for Cu^{2+} and $\gamma_\pm = 0.531$ for Co^{2+}.

Since $a_i = \gamma_i m_i$, then by Eq. (3.5) we have

$$E = \varepsilon_2 - \varepsilon_1 = 0.337 + 0.277 + 0.059 \log \frac{0.577 \times 0.05}{0.531 \times 1} = 0.54\ \text{V}$$

By Eq. (3.4)

$$\Delta G = -2 \times 23\,050 \times 0.54 = -25\,000\ \text{cal}$$

Investigators, when studying chemical reactions generally tend to theoretically determine their thermodynamic possibility, i.e.

compute ΔG_T for a reaction before it is conducted. If the initial state of a system is known, and the equilibrium constant has been determined by Eq. (3.2) or (3.3), then it is simple to determine ΔG_T for the reaction by Eq. (3.1) and, consequently, the direction in which it proceeds spontaneously. To find the equilibrium constant by Eq. (3.2) or (3.3), we must calculate the change in the standard Gibbs energy. It is convenient to do this using the equation

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ \tag{3.6}$$

where ΔH_T° = heat of the reaction in standard conditions at the temperature T

ΔS_T° = change in the standard absolute entropies of the reagents at the same temperature.

Equation (3.6) permits us to calculate the change in the Gibbs energy with the aid of the third law of thermodynamics and the heat of the relevant reaction because it includes the absolute entropies of the reagents calculated according to this law (see Chap. 2).

Usually the possibility of a reaction is assessed according to the sign of ΔG_T° not only in standard conditions, but also in any conditions. It follows from Eqs. (3.1) and (3.2) that

$$\Delta G_T = RT \ln \frac{a_{A_1'}^{\nu_1'} a_{A_2'}^{\nu_2'}}{a_{A_1}^{\nu_1} a_{A_2}^{\nu_2}} + \Delta G_T^\circ$$

For the sign of ΔG_T to be the reverse of that of ΔG_T°, the absolute value of the first term of this equation must become determining. At a high negative value of ΔG_T°, we can speak with certainty that the reaction is possible. For reactions with ΔG_T° close to zero or having low positive values (up to 5 kcal/mol), their possibility can be assessed after experimental verification [18].

If a reaction is conducted at 298.15 K, the value of ΔG_{298}° is determined from tables of standard thermodynamic quantities (Appendix 1).

Example 94. Determine whether the following reaction of cracking of hexadecane is possible at 298 K:

$$C_{16}H_{34}(lq) \rightleftarrows C_5H_{12}(g) + 2C_4H_8(g) + C_3H_6(g)$$

$$\text{n-pentane\quad isobutane\quad propylene}$$
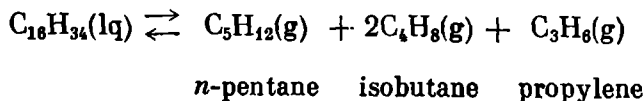
Solution. We find the required thermodynamic quantities, $(\Delta H_{298}^\circ)_{form}$ and S_{298}°, from Appendix 1:

	$C_{16}H_{34}$	C_5H_{12}	C_6H_8	C_3H_6
$(\Delta H_{298}^\circ)_{form}$, kcal/mol	−108.58	−35.00	−4.04	4.88
S_{298}°, cal/mol·K	148.10	83.40	70.17	63.80

$$\Delta H_{298}^\circ = -35.00 - 4.04 \times 2 + 4.88 + 108.58 = 70.38 \text{ kcal}$$

$$\Delta S_{298}^\circ = 83.40 + 70.17 \times 2 + 63.80 - 148.10 = 139.44 \text{ cal/K}$$

$$\Delta G_{298}^\circ = 70\,380 - 298 \times 139.44 = 28\,827 \text{ cal}$$

The decomposition of hexadecane into the products indicated above is impossible at 298 K.

Some tables of standard thermodynamic quantities [9, 56] give the Gibbs energy of formation of substances from simple compounds at any temperature $(\Delta G_T^\circ)_{form}$. In this case, ΔG_T° for a reaction will be

$$\Delta G_T^\circ = [\sum (\Delta G_T^\circ)_{form}]_{pr} - [\sum (\Delta G_T^\circ)_{form}]_r$$

Example 95. Will 1,2-dibromoethane be produced if ethylene is brominated at 298 K in the standard state:

$$C_2H_4(g) + Br_2(lq) \rightleftarrows C_2H_4Br_2(lq)$$
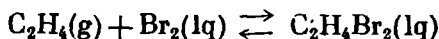
Solution. Appendix 1 gives $(\Delta G_{298}^\circ)_{form}$ equal to 16.282, 0, and −4.940 kcal/mol for $C_2H_4(g)$, $Br_2(lq)$, and $C_2H_4Br_2(lq)$. Hence,

$$\Delta G_{298}^\circ = -4.940 - 16.282 = -21.222 \text{ kcal}$$

Consequently, 1,2-dibromoethane can be produced in the conditions indicated above.

It is sometimes interesting to know the value of ΔG_T° for a reaction at any temperature. The relationship $\Delta G = f(T)$ is found by integration of the Gibbs-Helmholtz equation

$$\Delta G_T = \Delta H_T + T \left(\frac{\partial \Delta G}{\partial T} \right)_p$$

Introducing $\Delta H = f'(T)$ into this equation and integrating it, we get an explicit relationship $\Delta G = f(T)$. For reactions conducted in standard conditions in the gaseous phase, we have

$$\Delta G_T^\circ = \Delta H_0^\circ - \Delta a T \ln T - \frac{\Delta b}{2} T^2 - \frac{\Delta c}{6} T^3 + IT \qquad (3.7)$$

Equation (3.7) can be used to determine ΔG_T° when we know ΔH_0° for the reaction in question [the integration constant of Eq. (1.91)] and the integration constant of the given equation I. The value of I is determined with the aid of Eq. (3.7) if we know ΔG_T° for a given reaction for any temperature. Sometimes it can be calculated

according to the true chemical constants j (Table 3):

$I = -4.576\Delta j$

where $\Delta j = \sum j_{\text{pr}} - \sum j_{\text{r}}$.

TABLE 3

True Chemical Constants for Gases [8]

Substance	j	Substance	j	Substance	j
Br_2	$+2.57$	HBr	$+0.24$	I_2	$+3.08$
Cl_2	$+1.65$	HCl	-0.40	NH_3	-1.5
CH_4	-1.94	Hg	$+1.83$	N_2	-0.153
CO	-0.075	H_2	-3.68	N_2O	$+0.86$
CO_2	$+0.85$	HI	$+0.65$	NO	$+0.55$
		H_2O	-1.86	O_2	$+0.547$

Example 96. Determine the temperature dependence of ΔG_T° for the reaction of decomposition of ammonia in the gaseous phase

$$NH_3(g) = \frac{1}{2} N_2 + \frac{3}{2} H_2$$
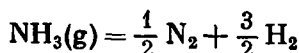
Solution. We take the required thermodynamic functions and the constants of the equation $C_p = \varphi(T)$ from Appendix 1:

	NH₃	N₂	H₂	Δ* for reaction
$(\Delta H_{298}^\circ)_{\text{form}}$, kcal/mol	-11.04	0	0	11.04
$(\Delta G_{298}^\circ)_{\text{form}}$, kcal/mol	-3.976	0	0	3.976
a	7.12	6.66	6.95	6.635
$b \times 10^3$ cal/mol·K	6.09	1.02	-0.2	-5.88
$c \times 10^6$	—	—	0.48	0.72

We calculate the integration constant of the Kirchhoff equation by Eq. (1.88):

$$\Delta H_0^\circ = \Delta H_{298}^\circ - \Delta a T - \frac{\Delta b}{2} T^2 - \frac{\Delta c}{3} T^3$$

$$\Delta H_0^\circ = 11\,040 - 6.635 \times 298 + \frac{5.88}{2} \times 10^{-3} \times 298^2 -$$

$$- \frac{0.72}{3} \times 10^{-6} \times 298^3 = 9416 \text{ cal}$$

---

* Here and below by Δ for a reaction, we mean the thermodynamic functions of the reaction calculated as the difference of the thermodynamic quantities indicated in the first column of the table with account taken of the stoichiometry of the reaction. For instance in the given case, we have $\Delta a = \frac{3}{2} \times 6.95 + \frac{1}{2} \times 6.66 - 7.12 = 6.635$, etc.

We find the integration constant I according to Eq. (3.7):

$$I = \frac{\Delta G_T}{T} - \frac{\Delta H_0^\circ}{T} + \Delta a \ln T + \frac{\Delta b}{2} T + \frac{\Delta c}{6} T^2$$

$$I = \frac{3976}{298} - \frac{9416}{298} + 6.635 \times 2.303 \log 298 - \frac{5.88}{2} \times 10^{-3} \times$$

$$\times 298 + \frac{0.72}{6} \times 10^{-6} \times 298^2 = 18.61$$

Thus, the temperature dependence of ΔG_T° is expressed by the equation

$$\Delta G_T^\circ = 9416 - 15.25 T \log T + 2.94 \times 10^{-3} T^2 - 0.12 \times 10^{-6} T^3 +$$

$$+ 18.61 T$$

It is convenient to use the Temkin-Schwartsman equation for determining ΔG_T° for a reaction at any temperature. It is obtained from the general relationship

$$\Delta G_T^\circ = \Delta H_T^\circ - T \Delta S_T^\circ$$

into which the following quantities are inserted:

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \int\limits_{298}^{T} \Delta C_p \, dT$$

$$\Delta S_T^\circ = \Delta S_{298}^\circ + \int\limits_{298}^{T} \frac{\Delta C_p}{T} \, dT$$

After integration and the grouping of terms containing Δa, Δb, and Δc, the Temkin-Schwartsman equation becomes

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ - T \left(\Delta a M_0 + \Delta b M_1 + \Delta c M_2 \right) \qquad (3.8)$$

where M_0, M_1, M_2 = constants of the equation depending on the temperature (Appendix 16)

ΔH_{298}° = standard heat of reaction at 298.15 K

ΔS_{298}° = difference between standard absolute entropies of products and reactants, $\Delta S_{298}^\circ = (\sum v_i' S_{298}^\circ)_{pr} - (\sum v_i S_{298}^\circ)_r$

Δa, Δb, Δc = algebraic sums of the coefficients of the relationship $C_p = \varphi(T)$, $\Delta a = (\sum v_i' a_i)_{pr} - (\sum v_i a_i)_r$, etc.

Equation (3.8) can be used with a varying degree of approximation.

In the first approximation, the quantity $\Delta C_p^\circ = \varphi(T)$ may be disregarded. The equation, therefore, becomes

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ \qquad (3.8a)$$

Example 97. Is the reaction of dehydrocyclization of *n*-octane to *p*-xylene at 800 K possible:

$$C_8H_{18}(g) \rightleftarrows \quad \overset{H_3C}{\underset{CH_3}{\diagdown}} \quad (g) + 4H_2$$
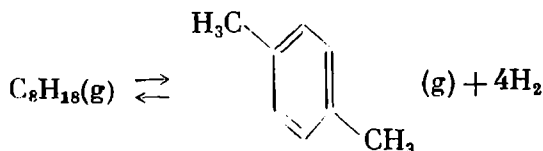
Solution. From tables of standard quantities (Appendix 1), we have

	n-C_8H_{18}	$C_6H_4(CH_3)_2$	H_2	Δ for reaction
$(\Delta H^\circ_{298})_{\text{form}}$, kcal/mol	−49.82	4.290	0	54.11
S°_{298}, cal/mol·K	111.55	84.23	31.211	97.524
a	1.651	−6.196	6.95	19.953
$b \times 10^3$ } cal/mol·K	177.317	145.716	−0.2	−32.4
$c \times 10^6$	−94.95	−83.786	0.48	13.084

For 800 K from Appendix 16, we have $M_0 = 0.3597$, $M_1 \times 10^{-3} = 0.1574$, and $M_2 \times 10^{-6} = 0.0733$.

By Eq. (3.8), we get

$$\Delta G^\circ_{800} = 54\,110 - 800 \times 97.524 - 800\,(0.3597 \times 19.953 -$$
$$- 0.1574 \times 32.4 + 0.0733 \times 13.084) = -26\,338 \text{ cal}$$

The reaction at 800 K is possible in the forward direction.
If we use Eq. (3.8a) for the calculations, then

$$\Delta G^\circ_{800} = 54\,110 - 800 \times 97.524 = -23\,909 \text{ cal}$$

i.e. the deviation of this value from that of ΔG°_{800} calculated by Eq. (3.8) is 9%.

Equation (3.8) is also convenient in that it permits us to calculate ΔG°_T for reactions for which the standard thermodynamic functions are not known for all the reagents. The lacking thermodynamic functions are calculated by the method of introducing corrections for the substitution of hydrogen by $-CH_3$ and other groups (see Sec. 1.3.8).

Example 98. Can α-methylstyrene be formed upon the alkylation of benzene with methylacetylene in standard conditions at 500 K:

$$C_6H_6(g) + CH_3 - C \equiv CH(g) \rightleftarrows \quad \overset{-C=CH_2(g)}{\underset{CH_3}{|}}$$
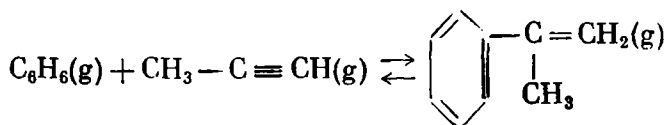
Solution. For C_6H_6 and CH_3—C≡CH, we take the thermodynamic functions from Appendix 1, and for α-methylstyrene we calculate them using the method of corrections, which we take from Appen-

dix 7. The sequence of introducing the corrections to the values for the main compound (benzene) is given in the following table.

Compound	$(\Delta H^\circ_{298})_{form},$ kcal/mol	$S^\circ_{298},$ cal/mol·K	a	$b \times 10^3$	$c \times 10^6$
			cal/mol·K		
Benzene	19.82	64.34	—4.2	91.3	—36.63
First substitution	—7.87	12.08	0.78	16.68	—5.41
Second substitution: type numbers (A, B)					
1,5	—4.68	10.76	1.09	18.71	—7.16
ditto, 2,5	—6.18	6.72	0.37	19.25	—7.72
Double bond in position					
1=3	28.23	—0.11	2.18	—15.62	6.42
α-Methylstyrene	29.32	93.79	0.22	130.32	—50.50

Next we perform the calculations similar to Example 97.

On the basis of tables of standard thermodynamic quantities and the values found above, we calculate the change in the thermodynamic functions of the reaction:

	C_6H_6	$CH_3-C\equiv CH$	$C_6H_5\overset{\underset{\displaystyle CH_3}{\vert}}{C}=CH_2$	Δ for reaction
$(\Delta H^\circ_{298})_{form},$ kcal/mol	19.82	44.32	29.32	—34.82
$S^\circ_{298},$ cal/mol	64.34	59.30	93.79	—29.85
a	—8.102	4.41	0.22	3.912
$b \times 10^3$ } cal/mol·K	112.78	37.61	130.32	—20.07
$c \times 10^6$	—71.306	14.38	—50.50	6.426

From Appendix 16, we have $M_0 = 0.1133$, $M_1 \times 10^{-3} = 0.0407$, and $M_2 \times 10^{-6} = 0.0149$.

Hence by Eq. (3.8), we get

$$\Delta G^\circ_{500} = -34\,820 + 500 \times 29.85 - 500\,(0.1133 \times 3.912 -$$

$$-0.0407 \times 20.07 + 0.0149 \times 6.426) = -19\,756 \text{ cal}$$

Since $\Delta G^\circ_{500} < 0$, then α-methylstyrene can form in the given conditions.

The thermodynamic functions of substances can be calculated by methods of quantum statistics. We shall not consider them in detail, but will show how functions calculated by these methods permit us to determine the Gibbs energy of a reaction at any temperature, or the equilibrium constant. The method of quantum statistics is

used to calculate the standard reduced enthalpy $(H° - H_0°)/T$ and the standard reduced function of the Gibbs energy $\Phi = (G° - H_0°)/T$ (this is the name given to the energy which a mole of a substance has at a given temperature in the standard state in comparison with its store of energy at absolute zero related to the temperature T).

To calculate $\Delta G_T°$, we must know the reduced functions of the Gibbs energy for all the reagents and the heat of the reaction at absolute zero.* Hence,

$$\Delta G° = \Delta \left(\frac{G° - H_0°}{T} \right) T + \Delta H_0° = \Delta \Phi T + \Delta H_0° \qquad (3.9)$$

where

$$\Delta \left(\frac{G° - H_0°}{T} \right) = \sum \left(\frac{G° - H_0°}{T} \right)_{pr} - \sum \left(\frac{G° - H_0°}{T} \right)_{r}$$

Reference books sometimes omit the heats of formation of some substances at absolute zero, but they are known for other temperatures. The heat of a reaction at absolute zero can be calculated through the reduced enthalpies of the reagents and the heat of the reaction at the temperature T:

$$\Delta H_0° = \Delta H_T° - \Delta \left(\frac{H° - H_0°}{T} \right) T \qquad (3.10)$$

where

$$\Delta \left(\frac{H° - H_0°}{T} \right) = \sum \left(\frac{H° - H_0°}{T} \right)_{pr} - \sum \left(\frac{H° - H_0°}{T} \right)_{r}$$

Combining Eq. (3.9) with Eq. (3.3) of the standard isotherm of a reaction, we get an equation for calculating the equilibrium constant:

$$R \ln K_p = - \left[\Delta \left(\frac{G° - H_0°}{T} \right) + \frac{\Delta H_0°}{T} \right] \qquad (3.11)$$

A large summary of the reduced functions is given in |9|.

Example 99. Calculate the equilibrium constant for the reaction of conversion of methane with steam conducted in the gaseous phase

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$
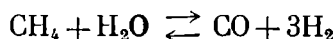
at 1000 K using Eq. (3.11).

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* For a reaction conducted in the gaseous phase, $\Delta H_0°$ is numerically equal to the integration constant of Eq. (1.88).

Solution. We find the required values of $(\Delta H_0')_{\text{form}}$ and $(G° - H_0°)/T$ for 1000 K from [9]. In calculating Δ for the reaction, we multipl; the values of the functions for hydrogen by three.

	CH₄	H₂O	CO	H₂	Δ for reaction
$(G° - H_0°)/T$, cal/mol·K	—47.65	—47.01	—48.860	—32.736	—52.40
$(\Delta H_0°)_{\text{form}}$, kcal/mol . .	—15.987	—57.107	—47.202	0	45.89

By Eq. (3.11), we get

$$\log K_p = -\frac{1}{4.576}\left(-52.408 + \frac{45\,892}{1000}\right) = 1.424$$

Example 100. Calculate the equilibrium constant for the reaction of synthesis of formic acid at 500 K:

$$H_2O(g) + CO \rightleftarrows HCOOH(g)$$
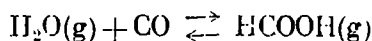
Solution. The value of $(\Delta H_0°)_{\text{form}}$ for formic acid is absent in [9]. Therefore, we calculate $\Delta H_0°$ for this reaction according to the reduced enthalpies:

	H₂O	CO	HCOOH	Δ for reaction
$(G° - H_0°)/T$, cal/mol·K	—41.293	—43.947	—56.158	29.082
$(H° - H_0°)/T$, cal/mol·K . . .	8.051	6.980	10.897	—4.134
$(\Delta H_{500}°)_{\text{form}}$, kcal/mol	—58.273	—26.295	—90.716	—6.148

By Eq. (3.10), we have

$$\frac{\Delta H_0°}{500} = -\frac{6148}{500} - (-4.134) = -8.162$$

and

$$\log K_p = -\frac{1}{4.576}(29.082 - 8.162) = -4.57$$

The experimentally found value of K_p at 491 K is 3.8 × 10⁻³.

It is sometimes interesting to know the temperature at which $\Delta G_T° = 0$. The empirical temperature dependence of the change in the Gibbs energy is most frequently used for such calculations:

$$\Delta G_T° = A + BT \tag{3.12}$$

It is assumed here that within the given temperature interval the change in the Gibbs energy of a reaction is a linear function of the temperature.

Equation (3.12) can be solved if we know its empirical coefficients A and B. To determine them, we must know $\Delta G_T°$ for a reaction at two temperatures.

Example 101. Calculate the temperature of equilibrium in standard conditions for the reaction of cracking of *n*-pentadecane

$$C_{15}H_{32}(g) \rightleftharpoons C_5H_{12}(g) + 2C_3H_6(g) + \quad C_4H_8(g)$$

2-butene (*cis*)
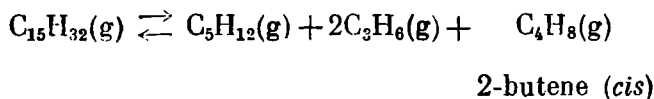
Solution. We use reference tables [9]. For each reagent, we write out from these tables the change in the Gibbs energy for their formation from simple compounds: $(\Delta G^\circ_{298})_{form}$ and $(\Delta G^\circ_{900})_{form}$.

	$C_{15}H_{32}$	C_5H_{12}	C_3H_6	C_4H_8	Δ for reaction
$(\Delta G^\circ_{298})_{form}$, kcal/mol	18.01	—2.00	14.99	15.74	25.71
$(\Delta G^\circ_{900})_{form}$, kcal/mol	241.30	71.46	39.10	56.25	—35.39

We compile a system of equations:

$$25.71 = A + 298B \quad \text{and} \quad -35.39 = A + 900B$$

Solution of these equations gives $A = 55.94$ and $B = -0.1015$. From Eq. (3.12) when $\Delta G^\circ_T = 0$, we have $T = -A/B$. Hence, $T = -55.94/-0.1015 = 551$ K. The reaction being considered is possible in the forward direction at a temperature above 551 K.

3.2
An Empirical Method for Calculating $(\Delta G^\circ_T)_{form}$ of Organic Compounds from Simple Substances

Several empirical methods have been proposed for calculating $(\Delta G^\circ_T)_{form}$ for compounds. They give results having different degrees of accuracy. The most complete summary of these methods and an appraisal of their accuracy are given in [46, 61, 62].

Let us consider the method proposed by D. van Krevelen and H. Chermin [62, 63]. They assume that

$$(\Delta G^\circ_T)_{form} = A + BT \tag{3.13}$$

The values of the coefficients A and B are found by summating the contributions for the groups which a given compound is divided into with account taken of a symmetry correction σ and corrections for the formation of rings and side branches of the main structure of a molecule. To improve the accuracy of the method. the values of A

and B are given for two temperature intervals: 300-600 K and 600-1500 K. The symmetry number σ corresponds to the number of identical space orientations which a molecule can have if it is assumed to be rigid and rotate about any of its axes or around any axis of the molecular structure [64]. The symmetry numbers for selected compounds are given in Table 4.

TABLE 4

Compound	σ	Compound	σ	Compound	σ
Ethane	6	1-Butylene	1	*p*-Xylene	4
Ethylene	4	1,3-Butadiene	2	1.3.5-Trimethyl-	
Acetylene	2	Cyclohexane	6	benzene	6
Propane	2	Benzene	12	Ethylbenzene	1
Propylene	1	*o*- and *m*-Xylenes	2	Butyl alcohol	1
n-Butane	2			Anthracene	4

Appendix 17 gives the values of A and B for the group contributions and corrections for the temperature intervals from 300 to 600 K and from 600 to 1500 K. Appendix 17a gives these quantities for alkanes, naphthenes, alkenes, alkynes, and aromatic hydrocarbons. When calculating the number of structural groups in the benzene ring or in an alkadiene with conjugated bonds, equal distribution of the electron pairs between adjacent carbon atoms or between carbon and a heteroatom is assumed; this is denoted by the symbol ↔. Thus, a benzene ring should be considered as consisting of six equivalent groups $HC\diagdown$. Appendix 17c gives the values of A and B for non-hydrocarbon groups.

Thus, the required value of $(\Delta G_T^\circ)_{\text{form}}$ will be

$$(\Delta G_T^\circ)_{\text{form}} = \sum \text{group contributions} + \sum \text{corrections} + RT \ln \sigma$$

The greatest deviation given by this method is from ± 3 to ± 5 kcal/mol when calculating $(\Delta G_T^\circ)_{\text{form}}$ for non-hydrocarbon compounds, and up to ± 1 kcal/mol for hydrocarbons.

Example 102. Using the method of van Krevelen and Chermin, calculate $(\Delta G_{700}^\circ)_{\text{form}}$ for *trans*-1,4-dimethylcyclohexane

$$H_3C\diagdown \quad \diagup\diagdown$$

$$CH_3$$
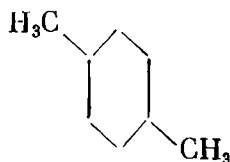
Solution. The given compound should be considered as consisting of four $\diagdown$CH$_2$ groups, two —CH groups, and two —CH$_3$ groups. In addition, account is taken of the correction for the formation of a six-membered ring and for branching in this ring in the *trans*-1,4 position. The symmetry number $\sigma = 4$. We enter all the values of the coefficients A and B and calculate the summary values of these coefficients in Table 5.

TABLE 5

Group	Group contributions, kcal/mol		No. of groups	Calculation of summary values, kcal/mol	
	A	$B \times 10^2$		A	$B \times 10^2$
—CH$_3$	—12.393	2.436	2	—24.786	4.872
$\diagdown$CH$_2$	—5.913	2.548	4	—23.652	10.192
—CH	—0.756	2.942	2	—1.512	5.884
Corrections:					
formation of ring				—1.145	—1.550
trans-1,4 (2,5) branch				—1.205	—0.286
$R \times 2.303$ log 4				—	0.274
Total for compound				—52.300	19.386

Thus, for *trans*-1,4-dimethylcyclohexane by Eq. (3.13), we have

$$(\Delta G_T^\circ)_{\text{form}} = -52.300 + 19.386 \times 10^{-2}T$$

For $T = 700$ K, we get $(\Delta G_{700}^\circ)_{\text{form}} = 83.402$ kcal/mol. The experimentally found value [9] is $(\Delta G_T^\circ)_{\text{form}} = 82.4$ kcal/mol.

Example 103. Determine $(\Delta G_T^\circ)_{\text{form}}$ for 2,5-dimethylpyridine

H$_3$C

at 500 K.

N CH$_3$
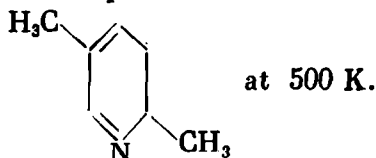
Solution. We find the corresponding values of the group contributions and corrections in Appendix 17, and enter them in the following table in which we perform the calculations.

Group	Group contributions, kcal/mol		No. of groups	Calculation of summary values, · kcal/mol	
	A	$B\times10^2$		A	$B\times10^2$
HC⤣	3.100	0.610	3	9.300	1.830
N⤣	11.320	1.11	1	11.320	1.11
—C⤣	5.280	0.994	2	10.560	1.988
—CH$_3$	—10.833	2.176	2	—21.666	4.352
Correction for branching of aromatic compounds in 1,4 position with respect to methyl radicals				—0.183	0.105
$\sigma=1$, $R\times2.303\log 1$				—	0
Total for compound				9.331	9.385

Consequently, for 2,5-dimethylpyridine, we have

$$(\Delta G_T^\circ)_{form} = 9.331 + 9.385 \times 10^{-2}T$$

whence

$$(\Delta G_{500}^\circ)_{form} = 9.331 + 9.385 \times 10^{-2} \times 500 = 56.256 \text{ kcal/mol}$$

3.3
Calculation of Equilibrium Constant

Having theoretically determined ΔG_T° for a reaction, we find the equilibrium constant from isotherm equation (3.2) which, if ΔG_T° is expressed in calories, can be written in the form

$$\log K_a = -\frac{\Delta G_T^\circ}{4.576T}$$

The value of $\log K_a$ for a reaction can be calculated according to the logarithms of the equilibrium constants for the reactions of formation of substances from simple compounds in standard conditions, $\log K_{form}$, given in reference books [9, 56].
For a reaction, we have

$$\log K_a = \left(\sum \log K_{form}\right)_{pr} - \left(\sum \log K_{form}\right)_r \qquad (3.14)$$

Example 104. Having calculated the equilibrium constants for the reactions listed below, which are possible in the cracking of *n*-eicosane, show what products will be contained in an equilibrium mixture at 800 K. The reactions proceed in the gaseous phase.

$$C_{20}H_{42} \rightleftarrows C_{12}H_{24} + n\text{-}C_8H_{18} \tag{a}$$

$$C_{20}H_{42} \rightleftarrows 4C_3H_6 + C_2H_6 + \underset{\text{3-hexene }(cis)}{C_6H_{12}} \tag{b}$$

$$C_{20}H_{42} \rightleftarrows C_6H_6 + 3H_2 + C_2H_4 + n\text{-}C_8H_{18} + C_4H_8 \tag{c}$$

$$C_{20}H_{42} \rightleftarrows n\text{-}C_6H_{14} + \underset{\text{isobutene}}{2C_4H_8} + \underset{\text{cyclohexane}}{C_6H_{12}} \tag{d}$$
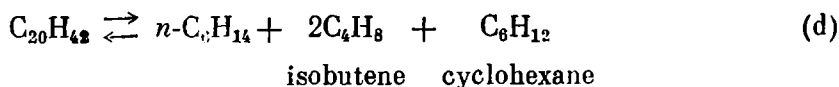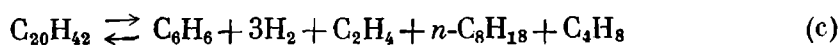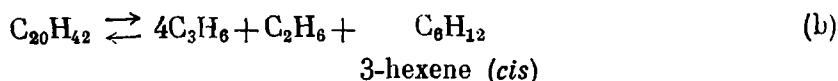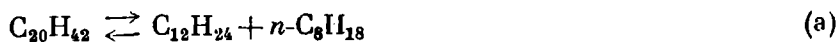
Solution. We write out the values of $-\log K_{\text{form}}$ at 800 K for all the components of the given system from [9]:

Compound	$C_{20}H_{42}$	$C_{12}H_{24}$	$n\text{-}C_8H_{18}$	C_3H_6	C_2H_6	$\underset{\text{3-hexene}(cis)}{C_6H_{12}}$	C_6H_6
$-\log K_{\text{form}}$	75.211	45.001	27.838	9.509	4.348	21.229	14.434

Compound	H_2	C_2H_4	$n\text{-}C_8H_{18}$	C_4H_8	$n\text{-}C_6H_{14}$	$\underset{\text{isobutene}}{C_4H_8}$	$\underset{\text{cyclohexane}}{C_6H_{12}}$
$-\log K_{\text{form}}$	0	6.690	27.838	12.974	19.964	12.974	20.451

Using Eq. (3.14), we get the following values of $\log K_a$ for reactions (a)-(d): 2.372, 11.863, 13.275, and 8.848, respectively.

The found values of $\log K_a$ show that the main direction of cracking is decomposition following reactions (b) and (c) into light hydrocarbons and H_2; therefore, the equilibrium mixture will mainly consist of H_2, C_3H_8, and C_4H_8.

In the experimental studying of reaction equilibrium, an empirical relationship $\log K = f(T)$ is often found in the form of a temperature series. These relationships also allow us to calculate $\log K$ for any temperature. Such relationships for various reactions encountered in petrochemical processes are given in [9].

Example 105. An equation of $\log K = f(T)$ of the following kind is given in [9] for the reaction of hydrogenation of isopropylbenzene:

$$\log K_p = \frac{9365.8}{T} - 10.707 \log T + 3.63 \times 10^{-3}T - 3.95 \times 10^{-7}T^2 + 9.8$$

Calculate $\log K_p$ for 510 K and compare the result with the experimentally found value of 0.916.

Solution. By the above equation, we have

$$\log K_p = \frac{9365.8}{510} - 10.707 \log 510 + 3.63 \times 10^{-3} \times 510 -$$

$$- 3.95 \times 10^{-7} \times 510^2 + 9.8 = 0.923$$

This value differs from the experimental one by 0.007.

The thermodynamic properties of very many organic substances have not been studied completely; therefore, it is sometimes necessary to resort to approximate methods for determining the equilibrium constants of reactions. The reliability of these methods was assessed by V. Kireev [17]. He also proposed a method of calculating the equilibrium constants for single-type reactions. By single-type reactions are meant such two reactions in which for each component of one reaction there is a component of the same type or an identical component in the other reaction. The single-type reaction method gives the best results for organic compounds when calculating the equilibrium constants of similar reactions of homologues if the same change in the number of moles is observed as a result of the reactions.

Using the subscripts 1 and 2 to denote the relevant quantities for two reactions, we can write

$$\Delta G_1^\circ = \Delta H_1^\circ - T \Delta S_1^\circ$$

$$\Delta G_2^\circ = \Delta H_2^\circ - T \Delta S_2^\circ$$

Single-type and similar reactions are characterized by the fact that the change in entropy in such reactions to a first approximation can be considered identical because the reagents are compounds of a similar structure. Hence, $\Delta S_1^\circ = \Delta S_2^\circ$ and

$$\Delta G_1^\circ - \Delta G_2^\circ = \Delta H_1^\circ - \Delta H_2^\circ$$

If we know the equilibrium constant for one reaction, we can find it for the other one as follows:

$$(\log K_p)_2 = (\log K_p)_1 + \frac{\Delta H_1^\circ - \Delta H_2^\circ}{4.576 T} \tag{3.15}$$

Verification of this equation has shown good coincidence between experimental and calculated data if the third or higher member of a homologous series is used for comparison. Comparison with the first two homologues gives considerable discrepancies.

Example 106. For the reaction of dehydrocyclization of *n*-nonane at 700 K, we have $\log K_p = 4.918$ [9]. Calculate the equilibrium constant for the reaction of dehydrocyclization of *n*-$C_{18}H_{38}$ according to which dodecylbenzene is formed.

Solution. We have the following reactions:

$$C_9H_{20}(g) \underset{\leftarrow}{\overset{\rightarrow}{=}} C_6H_5C_3H_7(g) + 4H_2$$

$$C_{18}H_{38}(g) \underset{\leftarrow}{\overset{\rightarrow}{=}} C_6H_5C_{12}H_{25}(g) + 4H_2$$
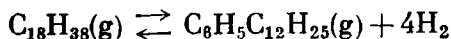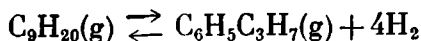
The heats of formation of the above compounds at 700 K are given in [9] (in kcal/mol):

Compound	C_9H_{20}	$C_6H_5C_3H_7$	$C_{18}H_{38}$	$C_6H_5C_{12}H_{25}$
$(\Delta H^\circ_{700})_{form}$	-64.92	-4.60	-117.61	-57.54

For the first reaction we have $\Delta H^\circ_{700} = 60.320$ kcal, for the second $\Delta H^\circ_{700} = 60.07$ kcal. By Eq. (3.15), we have

$$(\log K_p)_2 = 4.918 + \frac{60\,320 - 60\,070}{4.576 \times 700} = 4.996$$

Problems

173. In what direction will the reaction

$$CO + H_2O \underset{\leftarrow}{\overset{\rightarrow}{=}} CO_2 + H_2$$
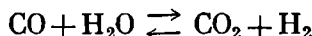
proceed at 1000 K if the initial composition of the gases (in mole per cent) is CO—10%, H_2O—25%, CO_2—3%, H_2—10%, and N_2—52%? At this temperature $K_p = 1.39$. The pressure in the system is 1 atm.

174. Will ethylbenzene be formed if the reaction of aromatization of *n*-octane is conducted at 600 K and 20 atm and if the molar ratio $H_2 : n\text{-}C_8H_{18} = 3 : 1$ in the initial mixture? At the given temperature we have $K_p = 39.54$.

175. In what direction will the reaction

$$C_3H_6 + H_2 \underset{\leftarrow}{\overset{\rightarrow}{=}} C_3H_8$$
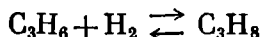
proceed at 298 K if the initial mixture consists of 30% of C_3H_6, 40% of H_2, 0.5% of C_3H_8, and 29.5% of N_2 (mole per cent)? Calculate the equilibrium constant using Eqs. (3.3) and (3.6). All the reagents are gases. The pressure in the system is 1 atm.

176. Will isopropyl chloride be formed according to the reaction

$$C_3H_8 + Cl_2 \underset{\leftarrow}{\overset{\rightarrow}{=}} C_3H_7Cl + HCl$$
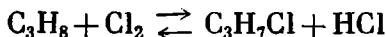
at 298 K and a pressure of 5 atm which is created by a nine-fold surplus of C_3H_8?

177. The equilibrium constant of the reaction

$$C_6H_5CH_3(g) + 3H_2 \underset{\leftarrow}{\overset{\rightarrow}{=}} C_6H_{11}CH_3(g)$$
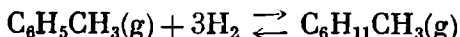
at 555 K is 0.646. The initial reaction mixture contains 23% of $C_6H_5CH_3$, 70% of H_2, and 7% of $C_6H_{11}CH_3$ (volume per cent).

The total pressure in the system is 1 atm. In what direction will the reaction proceed? How will the reaction be affected by dilution of the initial mixture by 50% with N_2?

178. Will chlorobenzene be formed at 298 K according to the reaction

$$C_6H_6(lq) + Cl_2(g) \rightleftarrows C_6H_5Cl(g) + HCl(g)$$
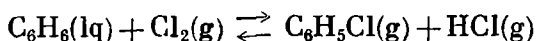
if the initial mixture consists of 10% by volume of HCl, saturated vapour of C_6H_6 (its vapour pressure at this temperature is 100 mm Hg), Cl_2 (its pressure is 40 times that of the benzene vapour), and nitrogen in an amount that raises the total pressure in the system to 10 atm?

179. A gas mixture containing 97 mole per cent of H_2O and 3 mole per cent of H_2 is heated to 1000 K. Will the equilibrium mixture react with nickel to form NiO? The relevant reactions are

$$Ni(c) + \frac{1}{2} O_2 \rightleftarrows NiO(c); \quad \Delta G^\circ_{1000} = -35{,}400 \text{ cal/mol}$$

$$H_2 + \frac{1}{2} O_2 \rightleftarrows H_2O(g); \quad \Delta G^\circ_{1000} = -45\,600 \text{ cal/mol}$$
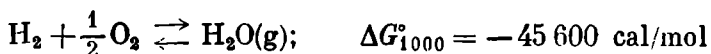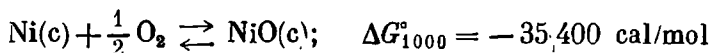
180. In what direction will electrochemical reactions proceed in the cell

$$Fe \,|\, Fe^{3+} \,\|\, Zn^{2+} \,|\, Zn$$
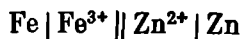
if the activity of the solution containing Fe^{3+} and that of the solution containing Zn^{2+} are 0.5 and 1.5, respectively?

181. Will the ion Sn^{2+} be oxidized in a cell formed of a calomel electrode with a saturated solution of KCl, and an oxidation-reduction electrode containing a 0.1M solution of $SnCl_2$ and a 0.002M solution of $SnCl_4$?

182. Determine the direction of the current in the external circuit for the cell

$$Zn \,|\, Zn^{2+} \,\|\, Cu^{2+} \,|\, Cu$$
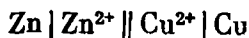
The electrodes are immersed in solutions whose molalities m for $ZnCl_2$ and $CuCl_2$ are 0.5 and 0.0005, respectively; $T = 298$ K. What is the work done by the cell?

183. Find the work of the cell

$$Pb \,|\, Pb(NO_3)_2 \,\|\, Co(NO_3)_2 \,|\, Co$$
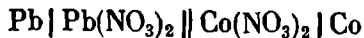
at 298 K. The molalities m of the solutions of $Pb(NO_3)_2$ and $Co(NO_3)_2$ are 0.01 and 0.5, respectively.

184. Determine whether the following reactions can proceed at 298 K in standard conditions in the gaseous phase. Use Eq. (3.6) to calculate ΔG°_{298}.

(1) $CH_3OH(g) \rightleftarrows HCHO + \frac{1}{2} H_2$

(2) $CH_3OH(g) \rightleftarrows CH_4 + \frac{1}{2} O_2$

(3) $CH_3OH(g) \rightleftarrows CO + 2H_2$

(4) $2CH_3OH(g) \rightleftarrows H_2 + HOCH_2CH_2OH(lq)$

(5) $2CH_3OH(g) \rightleftarrows C_2H_4 + 2H_2O(lq)$

(6) $CH_3OH(g) + NH_3 \rightleftarrows CH_3NH_2 + H_2O(lq)$

(7) $CH_3Cl(g) + NH_3 \rightleftarrows CH_3NH_2 + HCl(g)$

(8) $HCHO + NH_3 + H_2 \rightleftarrows CH_3NH_2 + H_2O(lq)$
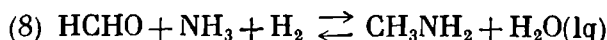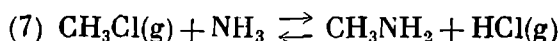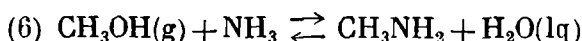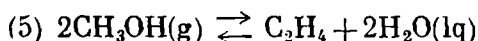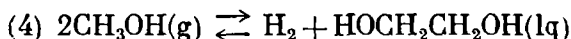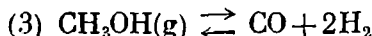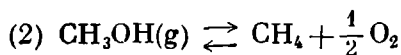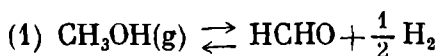
185. Using Eq. (3.7), determine whether the reaction of complete oxidation of methane

$$CH_4 + 2O_2 \rightleftarrows CO_2 + 2H_2O(g)$$
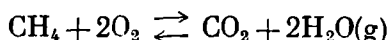
is possible at 600 K in standard conditions.

186. Is it possible to oxidize nitrogen in standard conditions at 1000 K according to the following reactions:

$$N_2 + \frac{1}{2} O_2 \rightleftarrows N_2O$$

$$\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightleftarrows NO$$
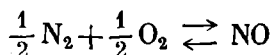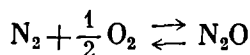
187. Use Eq. (3.8) to calculate ΔG_{700}° for the reaction

$$C_6H_{11}CH_3 \rightleftarrows C_6H_5CH_3 + 3H_2$$

Calculate $(\Delta H_{298}^{\circ})_{form}$, S_{298}°, and the coefficients of the relationship $C_p = \varphi(T)$ for methylcyclohexane according to the method of Anderson et al. The reaction proceeds in the gaseous phase.

188. The reaction

$$2NOCl(g) \rightleftarrows 2NO(g) + Cl_2(g)$$
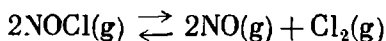
reaches equilibrium at 500 K and a total pressure of 1 atm when the partial pressure of the NOCl is 0.64 atm. Originally the system only contained NOCl. Calculate ΔG_{500}°. At what total pressure will the partial pressure of the chlorine be 0.5 atm?

189. The equilibrium constants of chemical reactions may have great or small values. The limiting value of the constant that can be determined experimentally is usually limited by the methods of

analysis. It has been found for a reaction of the type A $\rightleftharpoons$ B that the equilibrium mixture at 298 K contains less than 0.1 mole per cent of B. Calculate the minimum value of ΔG°_{298} for this reaction.

190. The following thermodynamic quantities were obtained for α- and β-pinenes at 298 K by measuring the heats of combustion and the heat capacities at low temperatures:

	$(\Delta H^{\circ}_{298})_{\text{form}}$, kcal/mol	S°_{298}, cal/mol•K
DL-α-pinene(lq)	-3.6 ± 0.3	70.95 ± 0.11
DL-β-pinene(lq)	-1.5 ± 0.3	69.48 ± 1.5

Calculate ΔG°_{298} and the equilibrium constant for the reaction

$$\text{DL-α-pinene(lq)} \rightleftharpoons \text{DL-β-pinene(lq)}$$
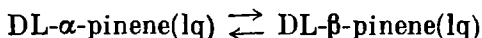
Indicate the errors in these quantities which are the result of the errors in the values of the thermodynamic quantities given above.

191. Using Eqs. (3.7), (3.8), (3.8a), and (3.9), calculate $(\Delta G^{\circ}_{800})_{\text{form}}$ for the reaction of formation of formic acid from simple substances. Compare the results with the value of $(\Delta G^{\circ}_{800})_{\text{form}} = -71\ 955$ cal given in [9].

192. Determine the direction in which the reaction

$$CH_4 + 3Cl_2 \rightleftharpoons CHCl_3 + 3HCl$$
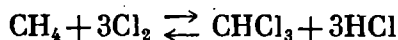
will proceed at 600 K with the aid of Eq. (3.8). The reaction is conducted in the gaseous phase in standard conditions.

193. Does urea form at 500 K according to the reaction

$$2NH_3(g) + CO_2 \rightleftharpoons (H_2N)_2CO(c) + H_2O(g)$$
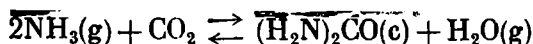
Calculate ΔG°_{500} by Eq. (3.8a).

194. Plot ΔG°_T against temperature for the reaction

$$CH_4 + 2H_2O(g) \rightleftharpoons CO_2 + 4H_2$$
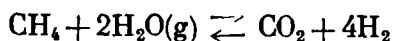
for the interval from 700 to 1500 K in the gaseous phase. Use Eq. (3.9) to calculate ΔG°_T for the reaction.

195. What is the value of ΔG°_{500} for the reaction

$$C_6H_5CH_3(g) + 2NO_2(g) \rightleftharpoons C_6H_3CH_3(NO_2)_2(g) + H_2$$
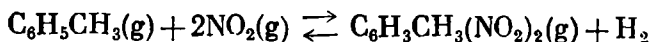
Use the method of Anderson et al to calculate the values of the thermodynamic quantities not given in the tables of standard values.

196. Which of the following reactions has the highest possibility in the process of pyrolysis of propane at 1000 K in standard con-

ditions:

(1) $C_3H_8 \rightleftarrows CH_4 + C_2H_4$

(2) $C_3H_8 \rightleftarrows H_2 + C_3H_6$

(3) $C_3H_8 \rightleftarrows CH_4 + C_2H_2 + H_2$

(4) $C_3H_8 \rightleftarrows 2H_2 + C_3H_4$ (methylacetylene)

(5) $C_3H_8 \rightleftarrows 2H_2 + C_3H_4$ (propadiene)

(6) $C_3H_8 \rightleftarrows 4H_2 + 3C$

197. At what temperature are the following reactions possible in standard conditions:
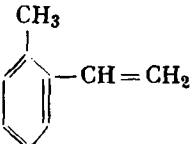
(1) $C_6H_6 + F_2 \rightleftarrows C_6H_5F + HF$

(2) $C_3H_6 + \frac{3}{2}O_2 \rightleftarrows CH_3CHO + HCOOH$

(3) $2CO + 4H_2 \rightleftarrows C_2H_5OH + H_2O$

(4) $C_3H_8 + 8Cl_2 \rightleftarrows (CCl_2)_2 + CCl_4 + 8HCl$

(5) $C_2H_2 + CH_3COOH \rightleftarrows HCOOH + C_3H_4$ (propadiene)

(6) $C_2H_2 + CH_3COOH \rightleftarrows 2H_2O + C_4H_2$ (diacetylene)

(7) $CO + 2H_2 \rightleftarrows CH_3OH$

(8) $C_6H_5CH_3 + C_2H_4 \rightleftarrows CH_3C_6H_4C_2H_5$ (1-methyl-4-ethylbenzene)

(9) $C_2H_2 + H_2O \rightleftarrows CH_3CHO$

(10) $2C_4H_8$ (isobutene) $+ H_2 \rightleftarrows C_8H_{18}$ (2,5-dimethylhexane)

(11) $C_5H_9C_5H_{11}$ (*n*-pentylcyclopentane) $\rightleftarrows$

$\rightleftarrows C_6H_5C_4H_9$ (*n*-butylbenzene) $+ 3H_2$.

198. Find the temperature at which the theoretical yield of acetylene in the process of pyrolysis of methane

$2CH_4 \rightleftarrows C_2H_2 + 3H_2$
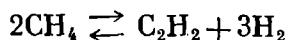
will be 20 mole per cent. The system is initially in the standard state.

199. Calculate $(\Delta G_T^\circ)_{form}$ for the compounds and temperatures indicated in the following table using the empirical method described in Sec. 3.2. Compare the calculated values with those given in reference books.

Compound	Formula	T, K	Known value of $(\Delta G_T^\circ)_{form}$, kcal/mol	Source
α-Methylstyrene	CH₃ ⬡—CH=CH₂	500	67.56	[2]
n-Hexyl alcohol	$CH_3(CH_2)_5OH$	298	—33.665	[9]
Acetaldehyde	CH_3CHO	500	—25.97	[9]
Thiocyclohexane	$C_5H_{10}S$	700	51.90	[9]
Fluorobenzene	C_6H_5F	500	—6.90	[9]
Benzothiol	C_6H_5SH	600	41.50	[9]
Pyrrolidine	C_4H_8NH	400	37.45	[9]

200. Find the temperature dependence of $(\Delta G_T^\circ)_{form}$ for the following compounds within the interval from 600 to 1500 K:

(1)

m-Vinylpyridine

(2)
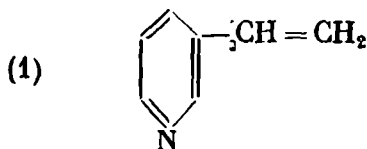
Methylenecyclopentadiene

(3)

m-Tolylaldehyde

(4)
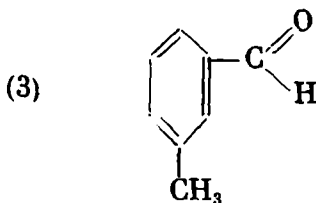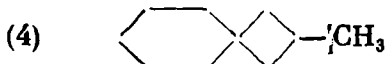
Methylcyclobutylcyclohexane

(5) $C_2H_5SO_2C_3H_7$
Ethylpropylsulphone

(6) $C_6H_5C_6H_{11}$
Phenylcyclohexane

(7) $C_6H_5C_6H_9$ (8) $C_6H_5C_6H_5$

       Phenylcyclohexene   Diphenyl

(9)

Monoethyl terephthalate
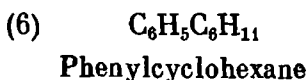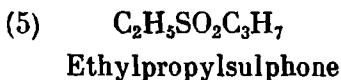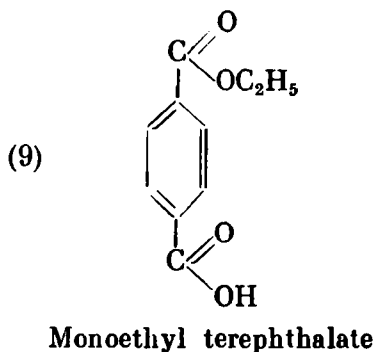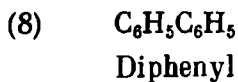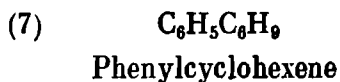
and also for the following compounds within the interval from 300 to 600 K:

(10) $C_6H_5CH_2C_6H_5$

       Diphenylmethane

(11)

Fluorene

(12)

Diphenylacetaldehyde

(13) $C_6H_5NHCOCH_3$

       Acetanilide

(14)

Piperazine

(15)

$$CH = CH - CHO$$
$$CH = CH - CHO$$

Muconic aldehyde

(16)

COOH
|

— OOCCH$_3$

Acetylsalicylic acid
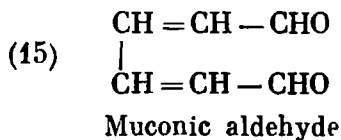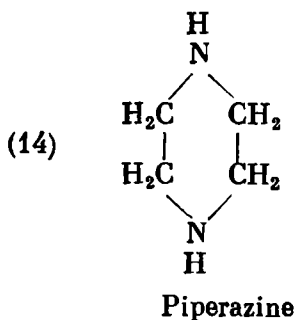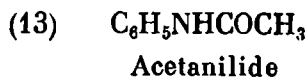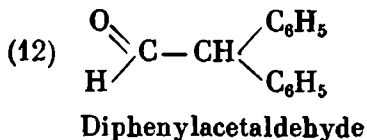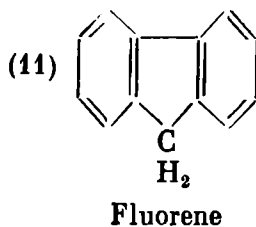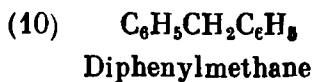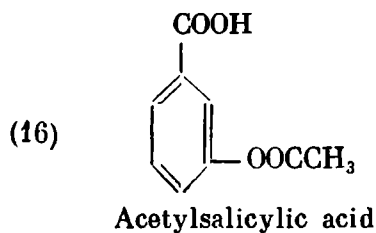
201. Calculate $(\Delta G^{\circ}_{400})_{form}$ for thymine
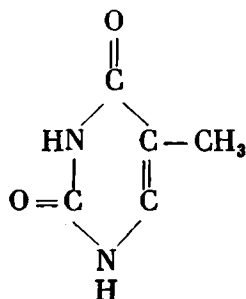
202. At what temperature is the hydrodesulphurizing of dithiaoctic acid possible:

$$\rightleftarrows CH_3(CH_2)_6COOH + 2H_2S$$
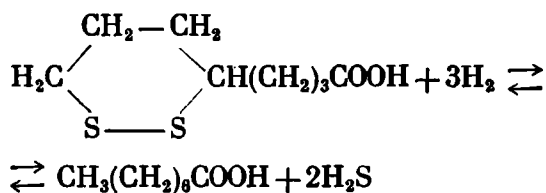
4

Calculation of Chemical Equilibrium in Ideal Gaseous Systems

4.1
Calculating Composition of Equilibrium Mixture When One Reaction Proceeds

A knowledge of the equilibrium constant of a reaction allows us to calculate the composition of an equilibrium mixture, i.e. to determine the maximum possible (theoretical) yield of the desired product.

The composition of an equilibrium mixture in a system is found by solving the equation of the law of mass action. Consider, for example, the reaction

$$A + 2B \rightleftarrows C$$
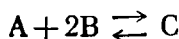
If it proceeds in the gaseous phase, and the gases may be considered ideal, the law of mass action for the reaction is

$$K_p = \frac{p_C}{p_A p_B^2} \tag{4.1}$$

where p_A, p_B, and p_C are the partial pressures of the relevant components in the equilibrium system.

The partial pressure of any component, according to Dalton's law, is

$$p_i = \frac{n_i}{\sum n_i} p = x_i p$$

where n_i = number of moles of the i-th component in the equilibrium mixture;

$\sum n_i$ = total number of moles of all the components of the mixture

p = total pressure in the system at the moment of equilibrium

x_i = mole fraction of the i-th component in the equilibrium system.

Introduction of the partial pressures expressed according to Dalton s law into the equation of the law of mass action yields

$$K_p = \frac{x_C}{x_A x_B^2 p^2} \tag{4.2}$$

Thus, the problem of determining the composition of an equilibrium mixture amounts to determining the mole fractions of its components because the total pressure in a system is usually known. When solving the problems relating to this section, remember that gases, regardless of the pressure in the system, are considered to be ideal. The equilibrium constant K_p, therefore, does not depend on the pressure.

The mole fractions of the components in an equilibrium mixture are related to the number of moles y of a reactant that have reacted by the moment when equilibrium sets in. There may be any number of moles of each of the reagents in the initial mixture. Thus, for the reaction

$$A + 2B \rightleftarrows C$$
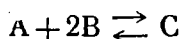
being considered, we assume that the number of moles in the initial mixture is $n_{0A} = a$, $n_{0B} = b$, and $n_{0C} = 0$. In the equilibrium mixture we thus have $n_A = a - y$, $n_B = b - 2y$, and $n_C = y$. The total number of moles in the equilibrium system is

$$\sum n_i = n_A + n_B + n_C = a + b - 2y$$

The mole fractions of the components in the system are

$$x_A = \frac{a - y}{a + b - 2y}, \quad x_B = \frac{b - 2y}{a + b - 2y}, \quad \text{and} \quad x_C = \frac{y}{a + b - 2y}$$

After introducing the expressions for x_i into Eq. (4.2), we get a cubic equation with respect to y:

$$K_p = \frac{y(a + b - 2y)^2}{(a - y)(b - 2y)^2 p^2}$$

We may sometimes get equations of fractional, the fourth, or higher powers. Such equations can be solved graphically or by methods of consecutive approximations.

If we assume that the initial mixture consists of a stoichiometric number of moles of the reactants, then y can be determined from the equation of the law of mass action with the aid of the auxiliary tables proposed by V. Korobov and A. Frost [24]. Appendix 18, which has been compiled in accordance with these tables and partly calculated by the authors of the present book, gives the solution for 30 different kinds of equations that in practice allow us to determine the composition of the equilibrium mixture for most types of reaction. We shall consider the use of the tables taking the reaction

$$A + 2B \rightleftarrows C$$

of the type considered above as an example.

According to the principle followed in constructing the tables, the number of moles in the initial mixture is $n_{0A} = 1$, $n_{0B} = 2$,

and $n_{0C} = 0$, and in the equilibrium mixture is $n_A = 1 - y$, $n_B = 2(1 - y)$, and $n_C = y$. The total number of moles in the equilibrium mixture is $\sum n = 3 - 2y$, and the mole fractions of the components in it are

$$x_A = \frac{1-y}{3-2y}, \qquad x_B = \frac{2(1-y)}{3-2y}, \qquad \text{and} \qquad x_C = \frac{y}{3-2y}$$

The final expression of the law of mass action for the given reaction is

$$K_p = \frac{y(3-2y)^2}{4(1-y)^3 p^2} \tag{4.3}$$

To determine y with the aid of Appendix 18, we divide Eq. (4.3) into a term depending on y (we shall denote it by M) and an independent term (K, p). We take logarithms of the resulting equation. For the case being considered, we have

$$K_p p^2 = M = \frac{y(3-2y)^2}{4(1-y)^3}$$

$$\log K_p + 2 \log p = \log M = \log y + 2 \log (3-2y) -$$
$$- 3 \log (1-y) - \log 4$$

which conforms to the 12th class of reactions indicated in Appendix 18.

Since K_p is known, and p is given, we can find $\log M$ and then determine y by interpolation, after which we can find the mole fractions of the components in the equilibrium mixture.

Other relationships may also be used in determining the number of moles in the initial and equilibrium mixtures. In this case, the sum of the number of moles in a mixture, the equation for the mole fraction, and, accordingly, the roots of the equation of the law of mass action will change. The composition of the equilibrium mixture expressed in mole fractions should be the same, however, no matter what designations are used for the number of moles in the initial mixture. For example for the same reaction, we can assume the following relationships:

$$A + 2B \rightleftharpoons C$$

In the initial mixture n_0 0   0   1

In the equilibrium mixture n . . . . . y $2y$ $1-y$ $\sum n = 1 + 2y$

Hence,

$$K_p = \frac{(1-y)(1+2y)^2}{4y^3 p^2} \tag{4.4}$$

In this case, we determine the roots of Eq. (4.4) according to Appendix 18 for the 8th class of reactions, taking into account that we know K_p for the reverse reaction.

Taking logarithms of Eq. (4.4), we get

$$\log K_p + 2 \log p = - \log M$$

We can also adopt the following designations.

$$A \quad + 2B \quad \rightleftarrows C$$

In the equilibrium mixture n . . . . . . $\dfrac{1}{3}y \quad \dfrac{2}{3}y \quad 1-y \quad \sum n = 1$

$$K_p = \frac{27\,(1-y)}{4y^3 p^2} \tag{4.5}$$

or

$$A \quad + \quad 2B \quad \rightleftarrows \quad C$$

In the equilibrium mixture n . . $\dfrac{1-y}{2} \quad 1-y \quad \dfrac{1}{2}y \quad \sum n = 1.5-y$

$$K_p = \frac{y\,(1.5-y)^2}{(1-y)^3\, p^2} \tag{4.6}$$

It is impossible to solve Eqs. (4.5) and (4.6) with the aid of the proposed tables.

Example 107. Calculate the composition of the gaseous equilibrium mixture in the reaction of dehydrocyclization of n-octane (oct) to p-xylene (xyl) at 500 K and 1 atm if $\log K_p = -2.077$. Express the composition in weight per cent.

Solution. We write the equation of the reaction and determine the number of moles in the systems:

$$C_8H_{18} \rightleftarrows (CH_3)_2C_6H_4 + 4H_2$$

Initial n_0 1   0   0

Equilibrium n . . . . 1$-y$ y $4y$ $\sum n = 1 + 4y$

The equation of the law of mass action is

$$K_p = \frac{p_{xyl}\,p_{hyd}^4}{p_{oct}}$$

The partial pressure of each component in the equilibrium system is

$$p_{xyl} = \frac{y}{1+4y}\,p, \quad p_{hyd} = \frac{4y}{1+4y}\,p, \quad \text{and} \quad p_{oct} = \frac{1-y}{1+4y}\,p$$

Hence,

$$K_p = \frac{256 y^5 p^4}{(1-y)\,(1+4y)^4}$$

Transformations yield

$$K_p p^{-4} = M = \frac{256 y^5}{(1-y)\,(1+4y)^4}$$

$$\log K_p - 4\,\log p = \log M$$

Since $p = 1$, we have $\log M = \log K_p = -2.077$. The reaction relates to the 10th class. From Appendix 18 we find that the required value is within the interval $0.10 < y < 0.20$.

We carry out linear interpolation for an approximate solution which gives us $y = 0.194$. For an accurate solution, the method of trial and error should be used within the established interval to find the value of y that actually satisfies the equation.

We find the composition of the equilibrium mixture of the system in mole fractions:

$$x_{oct} = \frac{1 - 0.194}{1 + 4 \times 0.194} = 0.454, \quad x_{hyd} = \frac{4 \times 0.194}{1 + 4 \times 0.194} = 0.437,$$

and $\quad x_{xyl} = \frac{0.194}{1 + 4 \times 0.194} = 0.109$

We use the following equation to calculate the weight per cents:

$$g_i = \frac{x_i M_i}{\sum (x_i M_i)} \times 100\%$$

$$g_{oct} = \frac{0.454 \times 114 \times 100}{0.454 \times 114 + 0.437 \times 2 + 0.109 \times 106} = 80.5\%,$$

$$g_{hyd} = 1.36\%, \quad \text{and} \quad g_{xyl} = 18.1\%$$

Example 108. The hydrodearomatization of n-propylbenzene (prop) to n-nonane (non) proceeds according to the equation

$$C_6H_5C_3H_7(g) + 4H_2 \rightleftarrows n\text{-}C_9H_{20}(g)$$
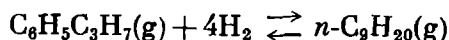
At 600 K we have $K_p = 65.02$. Calculate the composition of the equilibrium mixture if the initial mixture contains three times as much hydrogen as is needed stoichiometrically. The pressure $p = 1$ atm.

Solution. The number of moles in the system is:

	$C_6H_5C_3H_7$	H_2	$n\text{-}C_9H_{20}$
Initial n_0 . . .	1	12	0
Equilibrium n	$1 - y$	$12 - 4y = 4(3 - y)$	y

The total number of moles in the equilibrium system is $\sum n = 13 - 4y$. The expression of the law of mass action for the given relationship between the number of moles in the system is

$$K_p = \frac{y(13 - 4y)^4}{256(1 - y)(3 - y)^4 p^4}$$

We cannot determine y using Appendix 18 because the initial mixture has not been taken in a stoichiometric proportion. We therefore find y by trial and error: $y = 0.975$.

The composition of the equilibrium mixture in mole fractions is

$$x_{prop} = \frac{1 - y}{13 - 4y} = 0.002\overset{\cdot}{8}, \quad x_{hyd} = \frac{4(3 - y)}{13 - 4y} = 0.89,$$

and $\quad x_{non} = \frac{y}{13 - y} = 0.107$

4.2
Calculating Composition of Equilibrium Mixture When Several Parallel or Consecutive Reactions Proceed

A reaction may often proceed in several parallel directions with the formation of several products. This is most frequently observed when several isomers are formed as a result of such reactions as isomerization, dehydrogenation, alkylation, chlorination, and nitration. Sometimes the parallel proceeding of different reactions is possible, for instance dehydrogenation and isomerization. The composition of the equilibrium mixture in such a system includes all the substances participating in a reaction and formed as a result of it. The content of each of the substances in the equilibrium mixture is calculated according to the equilibrium constant for the relevant reaction.

Thus, the calculation of the composition of an equilibrium mixture when several reactions proceed concurrently in practice boils down to the solution of a system of equations whose number corresponds to the number of parallel reactions.

Example 109. Calculate the composition of the equilibrium mixture obtained in the isomerization of ethylbenzene at 600 K and 1 atm. The following parallel reactions are possible:

(I) $C_6H_5C_2H_5(g) \rightleftarrows$ (g)

(II) $C_6H_5C_2H_5(g) \rightleftarrows$ (g)

(III) $C_6H_5C_2H_5(g) \rightleftarrows$ (g)
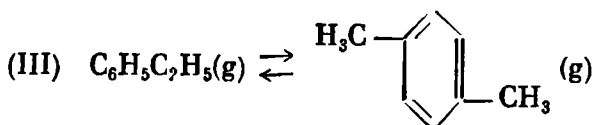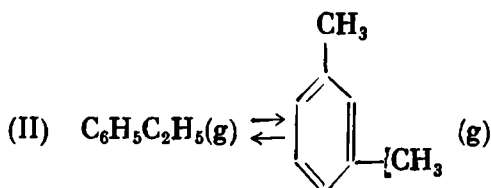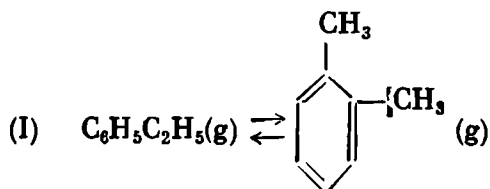
Solution. We find the values of $(\Delta G^{\circ}_{600})_{\text{form}}$ forming the system from a reference book [9]:

	$C_6H_5C_2H_5$	m-$C_6H_4(CH_3)_2$	o-$C_6H_4(CH_3)_2$	p-$C_6H_4(CH_3)_2$
$(\Delta G^{\circ}_{600})_{\text{form}}$, kcal/mol	57.646	55.099	56.103	56.060

We find the change in the Gibbs energy for each reaction like for the case of independent reactions:

(1) $(\Delta G^{\circ}_{600})_1 = 56.103 - 57.646 = -1.543$

(2) $(\Delta G^{\circ}_{600})_2 = 55.099 - 57.646 = -2.547$

(3) $(\Delta G^{\circ}_{600})_3 = 56.060 - 57.646 = -1.586$

We determine the equilibrium constants for the reactions on the basis of the formula $\log K_p = -\Delta G^{\circ}_T/4.576\,T$. We get $K_p^{I} = 3.66$, $K_p^{II} = 8.44$, and $K_p^{III} = 3.78$.

The number of moles in the system is:

	$C_6H_5C_2H_5$	m-$C_6H_4(CH_3)_2$	o-$C_6H_4(CH_3)_2$	p-$C_6H_4(CH_3)_2$
Initial n_0 ..	1	0	0	0
Equilibrium n	$1 - \sum y_i$	y_1	y_2	y_3

where $\sum y_i = y_1 + y_2 + y_3$.

The total number of moles in the equilibrium system is $\sum n_i = 1$.

The equations of the equilibrium constants for each of the reactions are:

$$K_p^{I} = \frac{p_{m\text{-xyl}}}{p_{\text{eth}}} = \frac{y_1}{1 - \sum y_i}$$

$$K_p^{II} = \frac{p_{o\text{-xyl}}}{p_{\text{eth}}} = \frac{y_2}{1 - \sum y_i}$$

$$K_p^{III} = \frac{p_{p\text{-xyl}}}{p_{\text{eth}}} = \frac{y_3}{1 - \sum y_i}$$

Each of the equations contains three unknowns, which we can find by solving the system of these equations. Summation yields

$$K_p^{I} + K_p^{II} + K_p^{III} = \frac{y_1 + y_2 + y_3}{1 - \sum y_i}$$

or

$$\sum K_p = \frac{\sum y_i}{1 - \sum y_i}$$

whence the unknown quantity in the above equation, $\sum y_i$, is

$$\sum y_i = \frac{\sum K_p}{\sum K_p + 1}$$

Since $\sum K_p = 3.66 + 8.44 + 3.78 = 15.88$, we have

$$\sum y_i = \frac{15.88}{15.88 + 1} = 0.9407$$

Consequently, $(1 - \sum y_i) = 1 - 0.9407 = 0.0593$, and

$$y_1 = K_{p,1}\left(1 - \sum y_i\right) = 3.66 \times 0.0593 = 0.217$$

$$y_2 = K_{p,2}\left(1 - \sum y_i\right) = 8.44 \times 0.0593 = 0.500$$

$$y_3 = K_{p,3}\left(1 - \sum y_i\right) = 3.78 \times 0.0593 = 0.224$$

and the composition of the equilibrium mixture is 5.9 % of $C_6H_5C_2H_5$, 21.7 % of $m\text{-}C_6H_4(CH_3)_2$, 50 % of $o\text{-}C_6H_4(CH_3)_2$, and 22.4 % of $p\text{-}C_6H_4(CH_3)_2$.

Example 110. The following reactions are possible when alkylating isobutane with 1-butene:

(I) $iso\text{-}C_4H_{10} + 1\text{-}C_4H_8 \rightleftarrows CH_3\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}CH_3$

2,2,3,3-tetramethylbutane

(II) $iso\text{-}C_4H_{10} + 1\text{-}C_4H_8 \rightleftarrows CH_3\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}CH_2\text{—}\overset{\displaystyle}{\underset{\displaystyle CH_3}{\overset{}{\underset{|}{CH}}}}\text{—}CH_3$

2,2,4-trimethylpentane
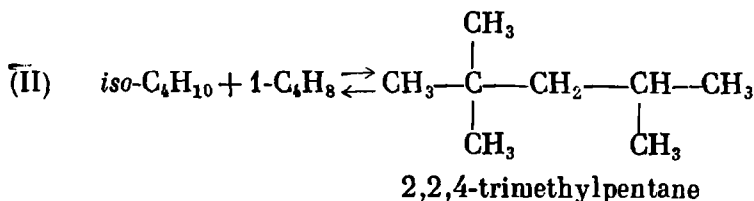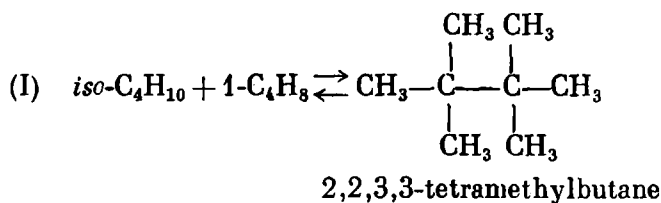
Calculate the composition of the equilibrium mixture at 500 K and 10 atm if the reactants are taken in equimolecular amounts. The reactions proceed in the gaseous phase.

Solution. We calculate the equilibrium constant of each reaction through the known values of $\log K_{form}$ [9] (at 500 K):

	$iso\text{-}C_4H_{10}$	$1\text{-}C_4H_8$	2,2,3,3-tetra-methylbutane	2,2,4-trimethyl-pentane
$\log K_{form}$	—6.2898	—11.7054	—20.530	—18.917

$$\log K_p^I = -20.530 - (-6.2898) - (-11.7054) = -2.535$$

$$\log K_p^{II} = -18.917 - (-6.2898) - (-11.7054) = -0.922$$

whence $K_p^I = 0.0029$ and $K_p^{II} = 0.1198$.

We assume the following composition of the system:

	iso-C_4H_{10}	1-C_4H_8	2,2,3,3-tetra-methylbutane	2,2,4-trimethyl-pentane
Initial n_0 . .	1	1	0	0
Equilibrium n	$1-y_1-y_2$	$1-y_1-y_2$	y_1	y_2

The total number of moles in the equilibrium system is $\sum n = 2 - \sum y_i$.

We write the expressions for the equilibrium constants:

$$K_p^{I} = \frac{y_1 \left(2 - \sum y_i\right)}{\left(1 - \sum y_i\right)^2 p}$$

$$K_p^{II} = \frac{y_2 \left(2 - \sum y_i\right)}{\left(1 - \sum y_i\right)^2 p}$$

Summation yields

$$\sum K_p = \frac{\sum y_i \left(2 - \sum y_i\right)}{\left(1 - \sum y_i\right)^2 p}$$

This equation is similar to that of K_p for the 11th class of reactions (Appendix 18), where $y = \sum y_i$. In our case, $\sum K_p = 0.1227$, $\log \sum K_p = -0.9112$, $\log M = 0.0888$, and $\sum y_i = 0.33$.

The composition of the equilibrium mixture (in mole fraction) is

$$x_{C_4H_{10}} = x_{C_4H_8} = \frac{1 - \sum y_i}{2 - \sum y_i} = \frac{1 - 0.33}{2 - 0.33} = 0.40 \text{ or } 40.0\%$$

We find the values of y_1 and y_2 from the following system of equations:

$$
\left.
\begin{aligned}
(1) & \quad y_1 + y_2 = \sum y_i \\
(2) & \quad \frac{y_1}{y_2} = \frac{K_p^{I}}{K_p^{II}}
\end{aligned}
\right\}
\quad y_2 = y_1 \frac{K_p^{II}}{K_p^{I}} \quad \text{and} \quad y_1 = \sum y_i \frac{K_p^{I}}{\sum K_p}
$$

whence

$$y_1 = 0.33 \times \frac{0.0029}{0.1227} = 0.0078 \quad \text{and} \quad y_2 = 0.0078 \times \frac{0.1198}{0.0029} = 0.322$$

Hence, for tetramethylbutane and trimethylpentane we have, respectively,

$$x = \frac{0.0078}{1.67} = 0.0046 \text{ or } 0.46\% \quad \text{and} \quad x = \frac{0.322}{1.67} = 0.195 \text{ or } 19.5\%$$

Example 111. The following reactions of alkylation and polymerization proceed in a reactor simultaneously at 500 K and 1 atm:

(1) $C_3H_6 + C_4H_{10} \rightleftarrows C_7H_{16}$ (2,3-dimethylpentane)

(2) $2C_3H_6 \rightleftarrows C_6H_{12}$ (1-hexene)
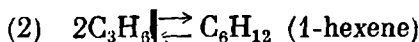
The equilibrium constants are $K_p^I = 34.5$ and $K_p^{II} = 7.19$. What is the theoretical yield if in one case one mole each of C_3H_6 and C_4H_{10} were taken for conducting the reactions, and in the other three moles of C_3H_6 and one mole of C_4H_{10}? The reaction proceeds in the gaseous phase.

Solution. We consider the first case. The number of moles in the systems is:

	C_3H_6	C_4H_{10}	C_7H_{16}	C_6H_{12}
Initial n_0	1	1	0	0
Equilibrium n	$1-y-z$	$1-y$	y	$\dfrac{z}{2}$

The total number of moles in the system is $\sum n = \dfrac{4-2y-z}{2}$.
The equilibrium constants are:

(1) $K_p^I = \dfrac{y(4-2y-z)}{2(1-y)(1-y-z)}$

(2) $K_p^{II} = \dfrac{z(4-2y-z)}{4(1-y-z)^2}$

Simultaneous solution of the equations allows us to determine the required values of y and z. We use the graphical method for this purpose. From the above equations, we find relationships $z = f(y)$ and plot them on a graph. We find the point of intersection of the two curves whose coordinates correspond to the required values of y and z.

We find the expression for z_1 from Eq. (1) and for z_2 from Eq. (2):

$$z_1 = \frac{2K_p^I(1-y)^2 - y(4-2y)}{2K_p^I(1-y) - y}$$

$$z_2 = \frac{-(4K_p^{II}+1)y + (4K_p^{II}+2)}{4K_p^{II}+1} \pm$$

$$\pm \sqrt{\left[\frac{(4K_p^{II}+1)y - (4K_p^{II}+2)}{4K_p^{II}+1}\right]^2 - \frac{4K_p^{II}(1-y)^2}{4K_p^{II}+1}}$$

We assign different values to y and use the above equations to calculate z_1 and z_2. We get the following results:

y	z_1	z_2
0.4	0.575	0.4·2
0.6	0.345	0.253
0.7	0.219	0.178
0.8	0.065	0.108
0.9	—0.215	0.041

After using the found values to plot $y = f(z_1)$ and $y = f'(z_2)$ (Fig. 7), we find that for our case $y = 0.75$ and $z = 0.145$.
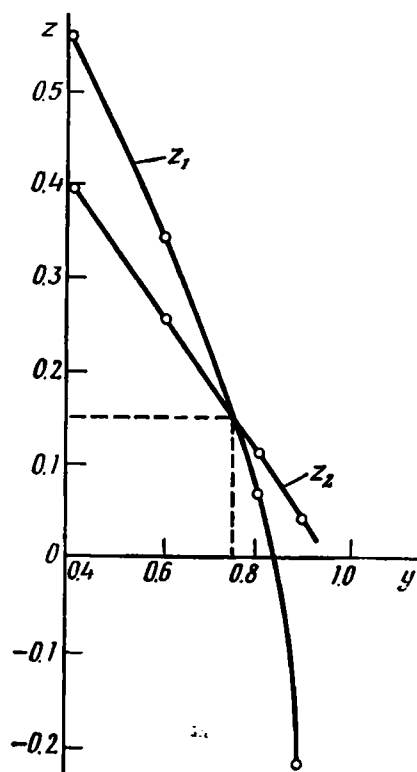
Fig. 7
Relationship $z_1 = f(y)$ and $z_2 = f'(y)$ for a graphical solution of simultaneous equations (Example 111, first case)

The composition of the equilibrium mixture for the first condition of our example is:

$$x = \frac{1-y-z}{2-y-\frac{z}{2}} = 0.09 \text{ for } C_3H_6$$

$$x = \frac{1-y}{2-y-\frac{z}{2}} = 0.212 \text{ for } C_4H_{10}$$

$$x = \frac{y}{2-y-\frac{z}{2}} = 0.635 \text{ for } C_7H_{16}$$

$$x = \frac{\frac{z}{2}}{2-y-\frac{z}{2}} = 0.061 \text{ for } C_6H_{12}$$

Let us consider the second case. The number of moles in the mixtures is:

	C_3H_6	C_4H_{10}	C_7H_{16}	C_6H_{12}
Initial n_0	3	1	0	0
Equilibrium n	$3-y-2z$	$1-y$	y	z

The equilibrium constants are:

$$(3) \quad K_p^I = \frac{y(4-y-z)}{(1-y)(3-y-2z)}$$

$$(4) \quad K_p^{II} = \frac{z(4-y-z)}{(3-y-2z)^2}$$

because the total number of moles in the system is $\sum n = 4-y-z$.

We also use the graphical method. We transform Eq. (3) to obtain z:

$$z_1 = \frac{K_p^I(3-y)(1-y)-y(4-y)}{2K_p^I(1-y)-y}$$

We find z_2 from the equation obtained by dividing Eq. (3) by Eq. (4):

$$\frac{K_p^I}{K_p^{II}} = \frac{y(3-y-2z)}{z(1-y)}$$

whence

$$z_2 = \frac{y(3-y)}{\dfrac{K_p^I}{K_p^{II}}(1-y)+2y}$$

We find the values of z_1 and z_2 for various values of y:

y	z_1	z_2
0.7	1.065	0.560
0.8	0.974	0.688
0.9	0.742	0.83
0.95	0.252	0.912

From Fig. 8 plotted according to these data, we find that the required values will be $y = 0.885$ and $z = 0.8$.

The composition of the equilibrium mixture for the second condition of our example is

$$x = \frac{3-y-2z}{4-y-z} = 0.221 \quad \text{for } C_3H_6$$

$$x = \frac{1-y}{4-y-z} = 0.05 \quad \text{for } C_4H_{10}$$

$$x = \frac{y}{4-y-z} = 0.383 \quad \text{for } C_7H_{16}$$

$$x = \frac{z}{4-y-z} = 0.345 \quad \text{for } C_6H_{12}$$

A comparison of the theoretically possible yields of the products of reactions I and II with different proportions of the reactants shows that we can suppress or increase the yield of selected products in concurrent reactions by changing the proportion of the reagents.

Fig. 8
Relationship $z_1 = f(y)$ and $z_2 = f'(y)$ for a graphical solution of simultaneous equations (Example 111, second case)

A product is sometimes obtained through the formation of one or more intermediates, i.e.it is possible to obtain the desired product through a number of intermediate reactions and according to the summary reaction. In calculating the composition of the equilibrium

mixture for such reactions, we must take into account that with commensurable values of the equilibrium constants of the intermediate reactions the equilibrium system will contain not only the products, but also intermediates. If the equilibrium constants of the intermediate reactions are not commensurable, then products of the reaction whose equilibrium constant is greater will predominate in the equilibrium mixture. For example:

(I) $A + B \rightleftarrows C$; K_p^I

(II) $C + B \rightleftarrows D$; K_p^{II}
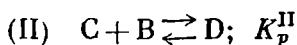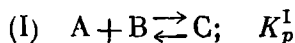
If $K_p^I \gg K_p^{II}$, then substance C will predominate in the equilibrium mixture, while if $K_p^{II} \gg K_p^I$, substance D will predominate. If $K_p^I \approx \approx K_p^{II}$, both C and D will be present in the equilibrium mixture.

Let us see how the composition of the equilibrium mixture is calculated for such a case.

Example 112. Calculate the composition of the equilibrium mixture obtained in the polymerization of propylene in the gaseous phase as follows:

$$2C_3H_6 \rightleftarrows n\text{-}C_6H_{12} \rightleftarrows C_6H_{12} \; (\textit{trans}\text{-2-hexene})$$

At 500 K for the first step, we have $K_p^I = 7.19$, and for the second step $K_p^{II} = 8.9$. The pressure in the system is 1 atm.

Solution. The number of moles in the systems is:

	C_3H_6	$n\text{-}C_6H_{12}$	*trans*-2-hexene
Initial n_0	2	0	0
Equilibrium n	$2(1-y)$	$y-z$	z

The total number of moles in the system is $\sum n = 2 - y$.
The equilibrium constant of the first step is

(1) $K_p^I = \dfrac{(y-z)(2-y)}{4(1-y)^2}$

and of the second step

(2) $K_p^{II} = \dfrac{z}{y-z}$

We find the values of y and z graphically. From Eq. (1) we get

$$z_1 = y - \frac{4K_p^I(1-y)^2}{2-y}$$

and from Eq. (2)

$$z_2 = \frac{K_p^{II} y}{K_p^{II} + 1}$$

We assign values to y and calculate the values of z_1 and z_2 corresponding to them:

y	z_1	z_2
0.8	—0.16	0.72
0.85	0.29	0.764
0.9	0.64	0.81
0.95	0.88	0.855
0.98	0.97	0.88

The relationships $z_1 = f(y)$ and $z_2 = f'(y)$ are shown in Fig. 9. The required values are $y = 0.94$ and $z = 0.85$.
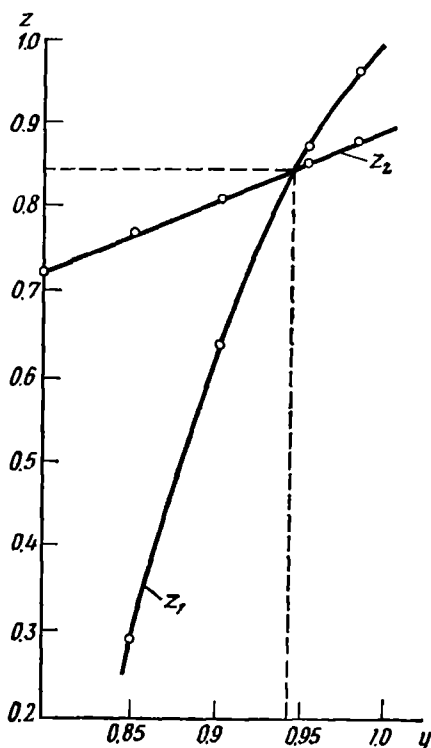
Fig. 9
Relationship $z_1 = f(y)$ and $z_2 = f'(y)$ for a graphical solution of simultaneous equations (Example 112)

The composition of the equilibrium mixture is

$$x = \frac{2(1-y)}{2-y} = 0.113 \text{ for } C_3H_6$$

$$x = \frac{y-z}{2-y} = 0.085 \text{ for } n\text{-}C_6H_{12}$$

$$x = \frac{z}{2-y} = 0.8 \text{ for } trans\text{-}2\text{-hexene}$$

Problems

203. Calculate the composition of the equilibrium mixture for the following reactions proceeding in the gaseous phase at the indicated temperature T and pressure p if the reactants are taken in stoichiometric amounts and the equilibrium constants are known.

Reaction	T, K	p, atm	$\log K_p$
(1) $C_6H_{11}CH_3 \rightleftarrows C_6H_5CH_3 + 3H_2$	600	1	1.27
(2) $C_6H_5CH_3 + 4H_2 \rightleftarrows C_7H_{16}$	700	10	-4.613
(3) $C_3H_6 + iso\text{-}C_4H_{10} \rightleftarrows CH_3 - CH - CH - CH_2 - CH_3$ $\qquad\qquad\qquad\qquad\quad\ \ \|\quad\ \|$ $\qquad\qquad\qquad\qquad CH_3\ \ CH_3$	600	2	0.014
(4) $C_6H_6 + C_3H_6 \rightleftarrows n\text{-}C_6H_5C_3H_7$	500	1	1.295
(5) $C_9H_{20} \rightleftarrows n\text{-}C_6H_5C_3H_7 + 4H_2$	700	1	4.718
(6) $3CH_3 - C \equiv CH \rightleftarrows C_6H_3(CH_3)_3$ 1,3,5-Trimethyl-benzene	1300	0.5	3.740
(7) $C_3H_6 + H_2O \rightleftarrows iso\text{-}C_3H_7OH$	500	15	-2.145
(8) $CH_3CHOHCH_3 \rightleftarrows CH_3COCH_3 + H_2$	464	1	-0.126
(9) $C_4H_8 + HCl \rightleftarrows C_4H_9Cl$	400	0.5	1.15
(10) $C_2H_2 + 2HCl \rightleftarrows C_2H_4Cl_2$	500	2	2.941
(11) $CH_4 + NH_3 \rightleftarrows HCN + 3H_2$	900	0.4	-2.361
(12) $C_3H_6 + CO + H_2 \rightleftarrows (CH_3)_2CHCHO$	500	5	0.192
(13) $2C_5H_{10} \rightleftarrows C_{10}H_{20}$	400	1	2.617
(14) $2C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + 2H_2$	475	1	0.227
(15) $2C_2H_5OH \rightleftarrows C_4H_6 + 2H_2O + H_2$	400	1	-0.578

204. Calculate the yield of 1-butene in the following reactions in the gaseous phase at 400 K (the stoichiometric amount of the reactant is taken for the reaction):

(1) $C_4H_9SH \rightleftarrows C_4H_8 + H_2S$, $\quad p = 2$ atm

(2) $2C_2H_4 \rightleftarrows C_4H_8$, $\qquad\qquad p = 15$ atm

(3) $C_4H_{10} \rightleftarrows C_4H_8 + H_2$, $\qquad p = 0.01$ atm
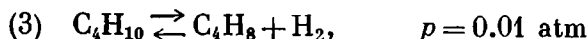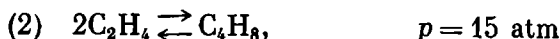
205. Determine the yield of methane at 800 K and 5 atm for the reaction

$$CO_2 + 4H_2 \rightleftarrows 2H_2O(g) + CH_4$$
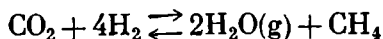
Use Eq. (3.8) to calculate ΔG°_{800}. The initial mixture contains one mole of CO_2 and four moles of H_2.

206. Calculate the yield of butadiene in the reaction

$$C_2H_5OH(g) + CH_3CHO(g) \rightleftarrows C_4H_6(g) + 2H_2O(g)$$
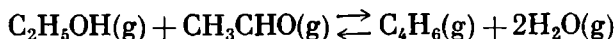
at 600 K and 0.5 atm if one mole each of the alcohol and acetaldehyde are taken for the reaction. Find ΔG°_{600} by Eq. (3.9).

207. Determine the theoretically possible yield of acetaldehyde at 500 K and 10 atm according to the reaction

$$C_3H_6(g) + \frac{3}{2}O_2 \rightleftarrows CH_3CHO(g) + HCOOH(g)$$
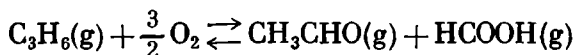
The initial mixture is taken in the stoichiometric proportion.

208. What is the theoretical yield of dinitrotoluene at 500 K and 2 atm according to the reaction

$$C_6H_5CH_3(g) + 2NO_2 \rightleftarrows C_6H_3CH_3(NO_2)_2(g) + H_2$$
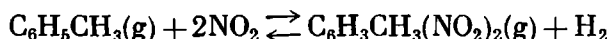
The initial mixture consists of one mole of toluene and two moles of nitrogen peroxide.

209. Calculate the composition of the equilibrium mixture obtained at 700 K and 2 atm for the reaction
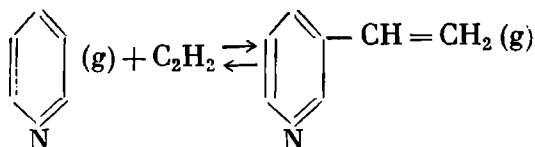
The initial mixture contains one mole each of pyridine and acetylene. Calculate the thermodynamic quantities not given in Appendix 1 according to the method of van Krevelen and Chermin.

210. What is the theoretical yield of the trimer of propylene (1-nonene) at 400 K and 1 atm? It is assumed that the trimer is formed directly from three moles of propylene taken for the reaction. The latter is conducted in the gaseous phase.

211. How much ethyl alcohol can be formed according to the reaction

$$CH_4 + CO + H_2 \rightleftarrows C_2H_5OH(g)$$
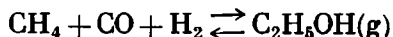
if it is conducted at 500 K and 30 atm? Consider the system to be ideal. The stoichiometric number of moles of the reactants is taken for the reaction.

212. The change in the Gibbs energy for the reaction

$$CO + Cl_2 \rightleftarrows COCl_2$$
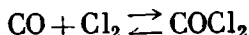
can be found by the equation

$$\Delta G_T = -24\,100 + 4T \ln T + 3.5T$$

Calculate the partial pressure of the chlorine in equilibrium with the phosgene at 600 K and a total pressure of 1 atm assuming that the gases are ideal.

213. The equilibrium constant $K_p = 5.5$ for the reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2$$
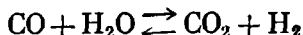
at 800 K. What will the mole fraction of the water in the equilibrium system be if a mixture of one mole of CO and five moles of $H_2O(g)$ is passed over the catalyst at this temperature?

214. To avoid polymerization in the alkylation of benzene with propylene, the reaction is conducted in the presence of an excess amount of the benzene. Determine the theoretical yield of cumene if the reaction is conducted at 600 K in the gaseous phase, the pressure in the system is 5 atm, and the initial mixture contains three moles of benzene per mole of propylene. In these conditions $K_p = 10$.

215. Calculate the theoretical yield of ethylcyclohexane prepared by the hydrogenation of ethylbenzene at 550 K and a total pressure of 1 atm if the initial mixture contains two moles of ethylbenzene and three moles of hydrogen. The temperature dependence of the equilibrium constant is expressed by the equation obtained by A. Vvedensky and his collaborators [9]:

$$\log K_p = \frac{10\,970}{T} - 20.526 \pm 0.088$$

The reaction is conducted in the gaseous phase.

216. How will the yield of methane in the reaction

$$CO_2 + 4H_2 \rightleftarrows 2H_2O + CH_4$$
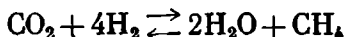
conducted at 800 K be affected by the fact that the initial mixture is taken in the molar ratio of $CO_2 : H_2 = 1 : 2$ at a total pressure of 8 atm? Compare the result with the answer to Problem 205.

217. What yield of *n*-hexane can be expected in the hydrocracking of *n*-dodecane at 900 K if the initial mixture contains a triple surplus of hydrogen? The pressure in the system is 10 atm. At this temperature $K_p = 0.0835$. All the reagents are gaseous.

218. The temperature dependence of the equilibrium constant for the reaction of dehydrogenation of secondary butyl alcohol has the form

$$\log K_p = \frac{-2790}{T} + 1.51 \log T + 1.865$$

Find the composition of the equilibrium mixture obtained as a result of the reaction

$$C_2H_5CHOHCH_3(g) \rightleftarrows C_2H_5COCH_3(g) + H_2$$
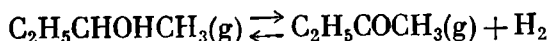
at 600 K when the initial mixture contains one mole each of the secondary butyl alcohol and H_2. The total pressure of the mixture is 2 atm.

219. The aromatization of *n*-hexane is conducted at 650 K and 10 atm, and the pressure is created by H_2 and *n*-C_6H_{14} taken in the molar ratio of 4 : 1. Determine the theoretical yield of the benzene. Consider the reagents to be ideal gases.

220. What yield of 1,2,4-trimethylcyclohexane is possible in the reaction

$$(CH_3)_3C_6H_3(g) + 3H_2 \rightleftarrows (CH_3)_3C_6H_9(g)$$

at 750 K, 10 atm and a triple surplus of H_2 in the mixture fed into the reactor compared with the stoichiometrically needed amount?

221. Determine the composition of the equilibrium gas mixture obtained in the process of isomerization of ethylbenzene to xylenes at 700 K and 1 atm if the equilibrium constants for the reactions are known:

$$C_2H_5C_6H_5 \rightleftarrows o\text{-}C_6H_4(CH_3)_2; \quad K_p = 2.68$$

$$C_2H_5C_6H_5 \rightleftarrows p\text{-}C_6H_4(CH_3)_2; \quad K_p = 2.58$$

$$C_2H_5C_6H_5 \rightleftarrows m\text{-}C_6H_4(CH_3)_2; \quad K_p = 5.74$$
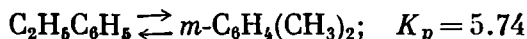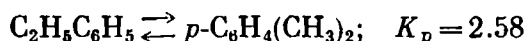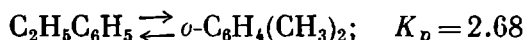
One mole of ethylbenzene has been taken for the reaction.

222. Using Eq. (3.9) to calculate ΔG_T° for the reaction, determine the composition of the equilibrium gas mixture in the process of isomerization of ethylcyclopentane at 700 K and 5 atm:

$$C_2H_5C_5H_9 \rightleftarrows C_5H_8(CH_3)_2 \quad \text{(1,1-dimethylcyclopentane)}$$

$$C_2H_5C_5H_9 \rightleftarrows C_5H_8(CH_3)_2 \quad \text{(1,2-}cis\text{-dimethylcyclopentane)}$$

$$C_2H_5C_5H_9 \rightleftarrows C_5H_8(CH_3)_2 \quad \text{(1,3-}trans\text{-dimethylcyclopentane)}$$
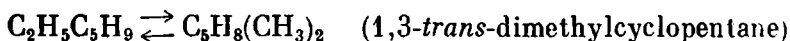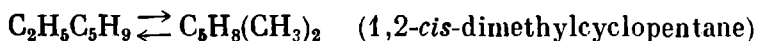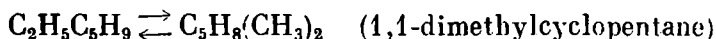
The initial mixture contains one mole of ethylcyclopentane.

223. Calculate the composition of the equilibrium gas mixture in the process of isomerization of one mole of 1,3-pentadiene at 700 K and 2 atm. The values of $(\Delta G_{700}^\circ)_{form}$ (in kcal/mol) are 73.21 for 1,2-, 59.38 for 1,3-, 63.66 for 1,4-, 73.27 for 2,3-pentadiene, 71.77 for 2-methyl-2,3-, and 59.46 for 2-methyl-1,3-butadiene.

224. Calculate the yield of aromatic hydrocarbons obtained in the process of aromatization of one mole of *n*-octane at 550 K and 1 atm

in the gaseous phase:

$$C_8H_{18} \underset{\longleftarrow}{\overset{\longrightarrow}{}} p\text{-}C_6H_4(CH_3)_2 + 4H_2; \quad K_p = 1.01$$

$$C_8H_{18} \underset{\longleftarrow}{\overset{\longrightarrow}{}} m\text{-}C_6H_4(CH_3)_2 + 4H_2; \quad K_p = 2.286$$

$$C_8H_{18} \underset{\longleftarrow}{\overset{\longrightarrow}{}} o\text{-}C_6H_4(CH_3)_2 + 4H_2; \quad K_p = 0.933$$

$$C_8H_{18} \underset{\longleftarrow}{\overset{\longrightarrow}{}} C_6H_5C_2H_5 + 4H_2; \qquad K_p = 0.207$$
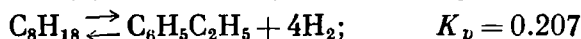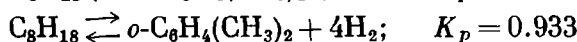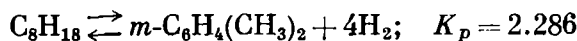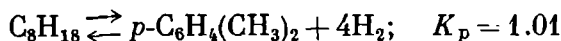
225. Determine the theoretically possible yield of butenes at 1000 K and 1 atm in the following concurrent reactions:

$$CH_3(CH_2)_2CH_3 \underset{\longleftarrow}{\overset{\longrightarrow}{}} 1\text{-butene} + H_2$$

$$CH_3(CH_2)_2CH_3 \underset{\longleftarrow}{\overset{\longrightarrow}{}} cis\text{-}2\text{-butene} + H_2$$

$$CH_3(CH_2)_2CH_3 \underset{\longleftarrow}{\overset{\longrightarrow}{}} trans\text{-}2\text{-butene} + H_2$$

$$CH_3(CH_2)_2CH_3 \underset{\longleftarrow}{\overset{\longrightarrow}{}} methyl\text{-}2\text{-propene} + H_2$$
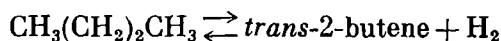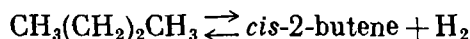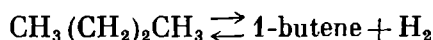
The initial reaction mixture contains one mole of n-butane.

226. Calculate the composition of the equilibrium mixture for the following concurrent reactions in the gaseous phase:

$$C_3H_8 \underset{\longleftarrow}{\overset{\longrightarrow}{}} 2H_2 + CH \equiv C - CH_3$$

$$C_3H_8 \underset{\longleftarrow}{\overset{\longrightarrow}{}} 2H_2 + CH_2 = C = CH_2$$
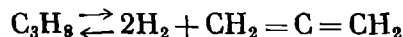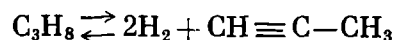
at 1000 K and 0.5 atm. Take one mole of propane for the reaction. Determine the equilibrium constant with the aid of Eq. (3.9).

227. Find the equilibrium composition of the mixture obtained in the hydrocracking of n-dodecane at 800 K and 20 atm. The initial gas mixture is equimolecular. The following products are formed:

$$C_{12}H_{26} + H_2 \underset{\longleftarrow}{\overset{\longrightarrow}{}} 2n\text{-}C_6H_{14}$$

$$C_{12}H_{26} + H_2 \underset{\longleftarrow}{\overset{\longrightarrow}{}} n\text{-}C_5H_{12} + n\text{-}C_7H_{16}$$

$$C_{12}H_{26} + H_2 \underset{\longleftarrow}{\overset{\longrightarrow}{}} n\text{-}C_4H_{10} + n\text{-}C_8H_{18}$$
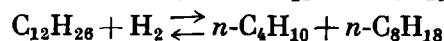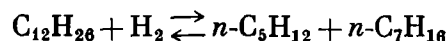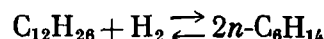
The values of $(\Delta G^\circ_{800})_{form}$ for the above substances are as follows (in kcal/mol):

Substance	$n\text{-}C_{12}H_{26}$	$n\text{-}C_4H_{10}$	$n\text{-}C_5H_{12}$	$n\text{-}C_6H_{14}$	$n\text{-}C_7H_{16}$	$n\text{-}C_8H_{18}$
$(\Delta G^\circ_{800})_{form}$	159.7	44.21	58.77	73.08	87.45	101.9

Consider the gases to be ideal.

228. Calculate the composition of the equilibrium mixture for the reaction of hydrocracking of n-tetradecane $C_{14}H_{30}$ at 850 K and 10 atm.

$$C_{14}H_{30}(g) + 2H_2 \underset{\longleftarrow}{\overset{\longrightarrow}{}} CH_4 + C_4H_{10} + n\text{-}C_9H_{20}(g); \quad \log K_p = 7.34$$

$$C_{14}H_{30}(g) + 2H_2 \underset{\longleftarrow}{\overset{\longrightarrow}{}} C_2H_6 + n\text{-}C_5H_{12} + n\text{-}C_7H_{16}(g); \quad \log K_p = 6.845$$

$$C_{14}H_{30}(g) + 2H_2 \underset{\longleftarrow}{\overset{\longrightarrow}{}} C_2H_6 + n\text{-}C_4H_{10} + n\text{-}C_8H_{18}(g); \quad \log K_p = 6.875$$
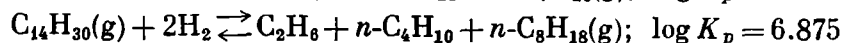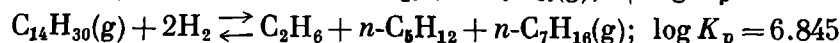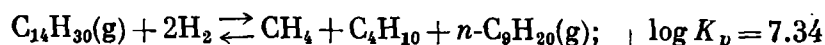
One mole of tetradecane and two moles of hydrogen are taken for the reaction.

229. The following reactions proceed in the pyrolysis of propane:

$$C_3H_8 \rightleftarrows C_3H_6 + H_2$$

$$C_3H_8 \rightleftarrows C_2H_4 + CH_4$$
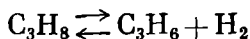
Using Eq. (3.9) to determine ΔG_T°, calculate the composition in equilibrium if the reaction is conducted at 1000 K and 1 atm in the gaseous phase.

230. Calculate the composition of the equilibrium mixture in the reaction of isomerization of one mole of 1-butene in the gaseous phase at 1 atm within the temperature interval from 400 to 900 K. Isomerization proceeds according to the equations

$$CH_2 = CH - CH_2 - CH_3 \rightleftarrows CH_3 - CH = CH - CH_3 \; (cis)$$

$$CH_2 = CH - CH_2 - CH_3 \rightleftarrows CH_3 - CH = CH - CH_3 \; (trans)$$

$$CH_2 = CH - CH_2 - CH_3 \rightleftarrows CH_2 = C \begin{smallmatrix} \diagup CH_3 \\ \diagdown CH_3 \end{smallmatrix}$$
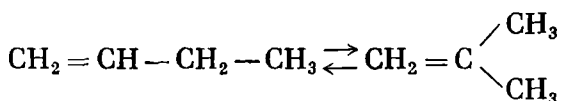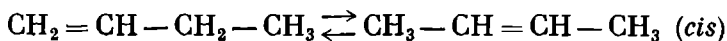
Use the results to plot a graph of the temperature dependence of the equilibrium composition.

231. What yield of cumene and *p*-diisopropylbenzene can be expected if one mole of benzene is alkylated with one mole of propylene in the gaseous phase at 700 K and 5 atm? The reaction proceeds as follows:

$$C_6H_6 + C_3H_6 \rightleftarrows C_6H_5C_3H_7; \qquad K_p = 0.685$$

$$C_6H_5C_3H_7 + C_3H_6 \rightleftarrows C_6H_4(C_3H_7)_2; \quad K_p = 0.239$$
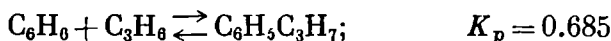
232. Determine the composition of the equilibrium mixture for the reaction of polymerization of two moles of propylene in the gaseous phase at 500 K and 1 atm. The reaction proceeds consecutively:

$$2C_3H_6 \rightleftarrows C_6H_{12}; \qquad K_p = 6.252$$

1-hexene

$$C_6H_{12} + C_3H_6 \rightleftarrows C_9H_{18}; \quad K_p = 6.152$$

1-nonene

5

Thermodynamic Calculation of Chemical Equilibrium in Real Gaseous Systems

There is no theoretically substantiated equation of state of real systems that would take into consideration the intermolecular forces of interaction and the volume of the molecules at any parameters. In practice, empirical equations are used to describe real systems. Their accuracy increases with a growth in the number of constants they contain. The use of these equations for thermodynamic descriptions of real systems results in complicated formulas and time-consuming calculations.

G. Lewis and M. Randall proposed to study real systems with the use of thermodynamic equations describing ideal systems in which the pressure for gases and the concentration for solutions are replaced with fictitious quantities—the fugacity and the activity, respectively. The *fugacity f* is a certain function of pressure whose introduction into the equations of thermodynamics describing ideal systems allows us to use them for describing real systems. The fugacity is proportional to the pressure:

$$f = \gamma p \tag{5.1}$$

where γ is the *fugacity coefficient* or, as it is more commonly called, the *activity coefficient* of a gas.

The activity coefficient γ has one strictly definite value at a given pressure. This postulate is based on our physical ideas of the ideal and real states of a system. At a low pressure, when $p \rightarrow 0$, the forces of interaction between the molecules of a gas in any real system are so small that we can assume the system to be ideal, i.e. that $f = p$, and, consequently, $\gamma = 1$. Such a definition of γ may be considered as its normalization. It characterizes the deviation of a gas from the ideal state. At a low pressure, when forces of attraction act between the molecules, we have $\gamma < 1$. At a high pressure, forces of repulsion act between the molecules, and $\gamma > 1$.

5.1

Methods of Calculating Fugacity

To calculate fugacity, we must know its explicit dependence on pressure at a constant temperature. The Gibbs energy is determined by the following equation as a function of pressure and temperature:

$$dG = -S \, dT + V \, dp$$

At $T = \text{const}$, we have

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{5.2}$$

For one mole of an ideal gas

$$G = RT \ln p + G_0 \, (T)$$

For one mole of a real gas

$$G = RT \ln f + G_0 \, (T) \tag{5.3}$$

Differentiation of Eq. (5.3) with respect to pressure at $T = \text{const}$ yields:

$$\left(\frac{\partial G}{\partial p}\right)_T = RT \left(\frac{\partial \ln f}{\partial p}\right)_T \tag{5.4}$$

Comparing Eqs. (5.2) and (5.4), we get

$$RT \left(\frac{\partial \ln f}{\partial p}\right)_T = V$$

and for $T = \text{const}$, we have

$$d \ln f = \frac{V}{RT} \, dp \tag{5.5}$$

Integration of Eq. (5.5) permits us to determine the fugacity at a given pressure if we can take an integral of the right-hand side of the equation for the given interval of pressures. The value of this integral can be found in several ways. Let us consider some of them.

5.1.1. Calculating the Fugacity According to the Volume Correction α for a Real Gas. The volume of a real gas V differs from that of an ideal gas V_{id} by the quantity α. Hence,

$$V = V_{\text{id}} - \alpha = \frac{RT}{p} - \alpha \tag{5.6}$$

Introducing Eq. (5.6) into (5.5), we get

$$d \ln f = \left(\frac{RT}{p} - \alpha\right) \frac{1}{RT} \, dp = d \ln p - \frac{\alpha}{RT} \, dp$$

Integration within the limits between states 1 and 2 yields

$$\ln\frac{f_2}{f_1} = \ln\frac{p_2}{p_1} - \int_{p_1}^{p_2} \frac{\alpha}{RT}\,dp$$

The value of the integral in the right-hand side of the equation is found graphically according to the area under the curve of $\alpha = \varphi\,(p)$ for the given pressure interval. The value of α is calculated according to Eq. (5.6). For this purpose, we must know from experiments the volume of one mole of a gas at the given pressure.

The fugacity at a definite pressure can be calculated if we take into consideration that when $p \to 0$, we have $f_1 = p_1$:

$$\ln f = \ln p - \frac{1}{RT}\int_0^p \alpha\,dp \tag{5.7}$$

The value of α at $p = 0$ is calculated with only a minor error by extrapolation along a straight line.

This method of determining the fugacity is the most reliable one because the value of the integral is found graphically according to the area confined by one curve plotted on the basis of experimental data.

It follows from Eq. (5.7) that

$$\ln\frac{f}{p} = \ln\gamma = -\frac{1}{RT}\int_0^p \alpha\,dp \tag{5.8}$$

The equation obtained permits us to calculate the activity coefficients for individual substances according to experimental data.

Example 113. Calculate the fugacity of isobutane at 373.15 K and a pressure of 10, 25, and 80 atm by using the following experimental data [65]:

p, atm	V, cm³/mol	p, atm	V, cm³/mol	p, atm	V, cm³/mol
1	30 914	20	134	60	126
3	10 060	25	132	80	123
5	5 852	30	130	90	112
10	2 680	40	129		
15	1 610	50	127		

Solution. We use the Clapeyron-Mendeleev equation to calculate V_{id}, and then find α by Eq. (5.6). The results of these calculations follow:

p, atm	V, cm³/mol	α, cm³/mol	p, atm	V, cm³/mol	α, cm³/mol	p, atm	V, cm³/mol	α, cm³/mol
1	30 600	—314	20	1 525	1 391	60	510	384
3	10 200	140	25	1 225	1 093	80	383	260
5	6 120	262	30	1 020	890	90	340	228
10	3 060	380	40	765	636			
15	2 040	430	50	612	486			

Figure 10 shows the relationship $\alpha = \varphi\,(p)$ for isobutane plotted according to the above data. The integral $\int_0^{10} \alpha\,dp$ corresponds to hatched area *1* with account taken of the sign of α. This area equals 1598 cm³·atm. Summation of hatched areas *1* and *2* gives us $\int_0^{25} \alpha\,dp =$
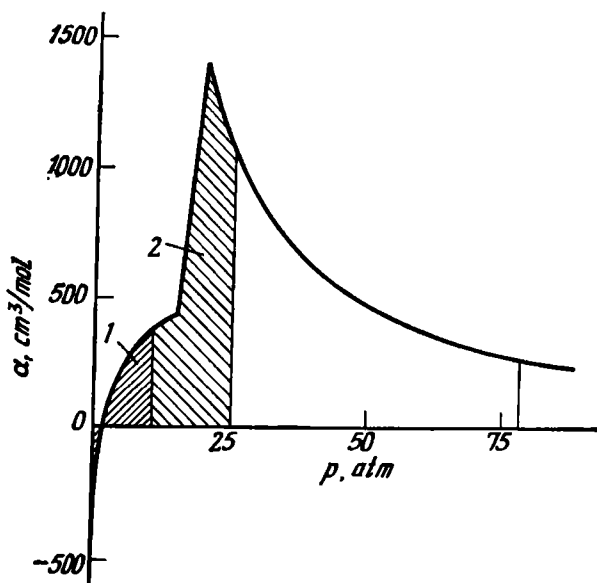
Fig. 10
Relationship $\alpha = \varphi\,(p)$ for isobutane at 373.15 K

$= 10\ 598\ \text{cm}^3 \cdot \text{atm}$. The total area under the curve gives us $\int\limits_{0}^{80} \alpha\, dp =$

$= 40\ 173\ \text{cm}^3 \cdot \text{atm}$.

According to Eq. (5.7), for $p = 10$ atm, we have

$$\log f_{10} = \log 10 - \frac{1598}{82 \times 373.15 \times 2.3} = 0.9773$$

and the fugacity is $f_{10} = 9.49$ atm.

For $p = 25$ atm, we get

$$\log f_{25} = \log 25 - \frac{10\ 598}{82 \times 373.15 \times 2.3} = 1.2469$$

and $f_{25} = 17.6$ atm.

For $p = 80$ atm, we have

$$\log f_{80} = \log 80 - \frac{40\ 173}{82 \times 373.15 \times 2.3} = 1.3321$$

and $f_{80} = 21.5$ atm.

5.1.2. Approximate Calculation of Fugacity. This method is based on the assumption that the correction α for the deviation of the volume of a real system from that of an ideal one does not depend on the pressure. This makes integration of Eq. (5.7) possible:

$$RT \ln f = RT \ln p - \alpha p$$

After involution, we get

$$\frac{f}{p} = \exp\left(-\frac{\alpha p}{RT}\right)$$

Expansion into a series gives

$$\exp\left(-\frac{\alpha p}{RT}\right) = 1 - \frac{\alpha p}{RT} + \cdots$$

Using only the first two terms of the series, we have

$$\frac{f}{p} = 1 - \frac{\alpha p}{RT} = \frac{p}{RT}\left(\frac{RT}{p} - \alpha\right) = \frac{p}{RT}\,V$$

The quantity $V/RT = 1/p_{\text{id}}$, where p_{id} is the pressure which a gas would have if it were ideal when occupying the given volume.

Thus, the equation for calculating the fugacity has the form

$$f = \frac{p^2}{p_{\text{id}}} \tag{5.9}$$

Example 114. Use Eq. (5.9) to calculate the fugacity of isobutane at 373.2 K, $p_1 = 10$, and $p_2 = 25$ atm if $V_{10} = 2680$ cm³/mol, and $V_{25} = 132$ cm³/mol.

Solution. For $p_1 = 10$ atm, we have

$$p_{\mathrm{id}} = \frac{RT}{V} = \frac{82 \times 373.2}{2680} = 11.4 \text{ atm}, \quad \text{and} \quad f = \frac{10^2}{11.4} = 8.77 \text{ atm}$$

For $p_2 = 25$ atm, we have

$$p_{\mathrm{id}} = \frac{82 \times 373.2}{132} = 231.8 \text{ atm}, \quad \text{and} \quad f = \frac{25^2}{231.8} = 2.7 \text{ atm}$$

A comparison of the results obtained with the values of the fugacity found by the graphical method shows that for a pressure of 10 atm the approximate method gives a value that is lower by 7.5%, while for a pressure of 25 atm the approximate method cannot be used to calculate the fugacity.

5.1.3. Calculations Using an Equation of State. If we know an equation of state for a real gas, it can be used to find $V = \varphi(p)$, and after integration of Eq. (5.5)—to determine the fugacity at a given pressure.

Let us consider the application of the van der Waals equation for calculating the fugacity. Since this equation has a simpler solution with respect to p, namely

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

we determine dp:

$$dp = \left[-\frac{RT}{(V-b)^2} + \frac{a}{V^3} \right] dV$$

We insert the value of dp into the basic equation (5.5):

$$RT \, d \ln f = -\frac{RTV}{(V-b)^2} \, dV + \frac{a}{V^2} \, dV$$

To determine the fugacity, the latter expression is integrated from $V^* \to \infty$ to V:

$$\ln \frac{f}{f^*} = \frac{b}{V-b} - \frac{b}{V^*-b} - \ln(V-b) + \ln(V^*-b) - \frac{2a}{RTV} + \frac{2a}{RTV^*}$$

Taking into account that when $V^* \to \infty$, we have $p \to 0$, $V^* - b = RT/p^*$, $p^* = f^*$, and $1/V^* = 0$, we obtain

$$\ln f = \ln \frac{RT}{V-b} + \frac{b}{V-b} - \frac{2a}{RTV} \tag{5.10}$$

In the above equations, the asterisk indicates that the relevant quantity relates to the ideal gaseous state of a substance.

Example 115. Use Eq. (5.10) to calculate the fugacity of isobutane at 373.2 K, $p_1 = 10$, and $p_2 = 25$ atm if $V_{10} = 2680$ cm³/mol, and $V_{25} = 132$ cm³/mol. The constants of the van der Waals equation for isobutane are $a = 12.876$ dm⁶·atm/mol² and $b = 0.114$ dm³/mol.

Solution.

$$\log f_{10} = \log \frac{0.082 \times 373.2}{2.680 - 0.114} + \frac{0.114}{(2.680 - 0.114)\,2.3} -$$

$$- \frac{2 \times 12.876}{0.082 \times 373.2 \times 2.680 \times 2.3} = 0.9591; \quad f_{10} = 9.10 \text{ atm}$$

$$\log f_{25} = \log \frac{0.082 \times 373.2}{0.132 - 0.114} + \frac{0.114}{(0.132 - 0.114)\,2.3} -$$

$$- \frac{2 \times 12.876}{0.082 \times 373.2 \times 0.132 \times 2.3} = 3.2123; \quad f_{25} = 1630 \text{ atm}$$

A comparison of the fugacities calculated by means of the van der Waals equation with the values found by the graphical method shows that for a pressure of 10 atm the fugacity is lower by 4.0%, while for a pressure of 25 atm this method cannot be used.

5.1.4. Calculations According to the Activity Coefficient. On the basis of the principle of corresponding states, we know that at the same reduced pressure $\pi = p/p_{cr}$ and the same reduced temperature $\tau = T/T_{cr}$ a number of properties of various substances are identical.

The relationship $\gamma = \varphi\,(\pi,\,\tau)$ is shown in Fig. 11. Here each curve corresponds to $\gamma = \varphi\,(\pi)$ at $\tau = \text{const}$. To use the given graph
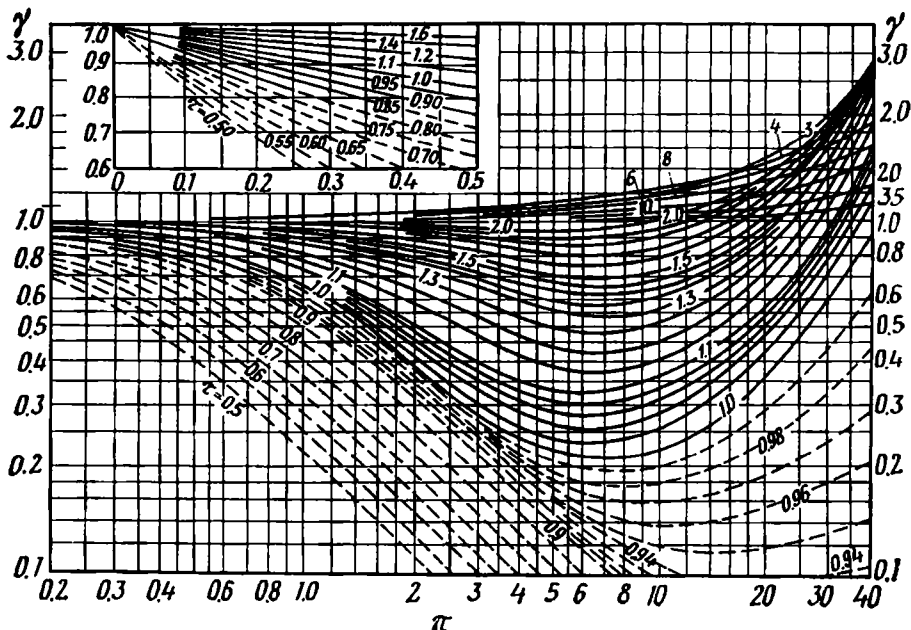
Fig. 11
Dependence of fugacity coefficient γ on reduced pressure π and reduced temperature τ (according to Newton and Dodge)

for calculating the fugacity of hydrogen, helium, and neon, their reduced pressure and temperature are calculated according to the pseudocritical parameters

$$\pi = \frac{p}{p_{cr}+8} \quad \text{and} \quad \tau = \frac{T}{T_{cr}+8}$$

R. Newton and B. Dodge based this method on experimental results obtained for easily liquefied light hydrocarbons. A. Lydersen and O. Hougen [45] in developing Newton's method showed that
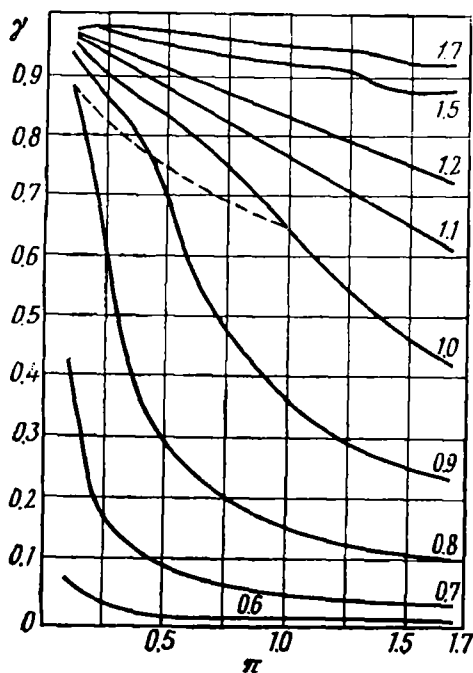
Fig. 12
Fugacity coefficients for selected liquids and gases at $Z_{cr} = 0.23$
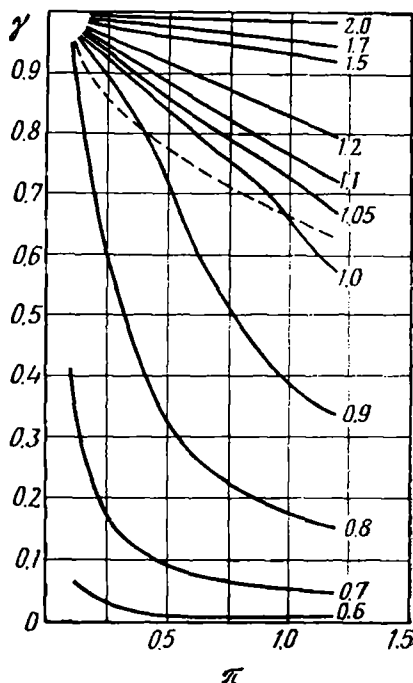
Fig. 13
Fugacity coefficients for selected liquids and gases at $Z_{cr} = 0.25$

Fig. 11 cannot be used to determine the activity coefficient for such systems in which the formation of a saturated vapour is possible ($\pi < 1$, $\tau < 1$).

It follows from the concept of a corresponding state that the compression factor Z, which takes into account the degree of deviation of a real system from an ideal one, must be the same for all substances in the critical state:

$$Z_{cr} = \frac{p_{cr}V_{cr}}{RT_{cr}}$$

Actually, however, its value also depends on the nature of the substance. All substances can be divided into four groups according to the value of Z_{cr}: (1) $Z_{cr} = 0.232$ —water, (2) $Z_{cr} = 0.24$ to 0.26 —ammonia, acetone, ethers, and alcohols, (3) $Z_{cr} = 0.26$ to 0.28 —60% of all substances (mainly hydrocarbons), and (4) $Z_{cr} = 0.28$ to 0.30 — oxygen, nitrogen, carbon monoxide, hydrogen sulphide, methane, ethane, and neon. Hydrogen and helium do not obey the generalized correlation in the region of saturation.
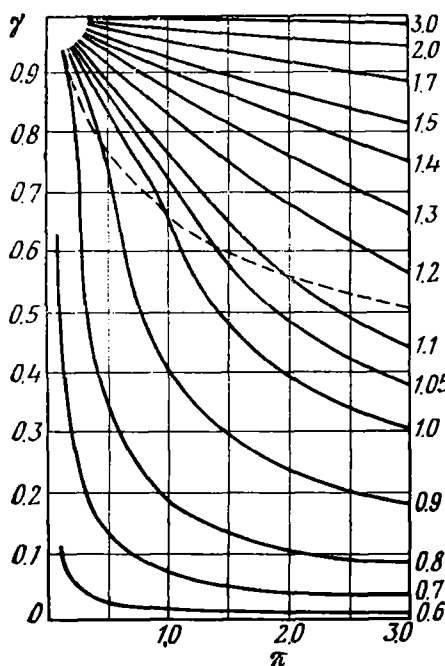
Thus, for the region close to the saturated state, we have $\gamma = \varphi$ (π, τ, Z_{cr}). As a result of verifying the relationship $p = f(V, T)$ for 72 different substances, Lydersen and Hougen compiled tables of $\gamma = \varphi(\pi, \tau, Z_{cr})$ (Appendix 19). We have used these tables to plot graphs of γ against π and τ for different values of Z_{cr} (Figs. 12-16). R. Reid and T. Sherwood [61] recommend tables (see Appendix 19) for determining the activity coefficients which in their opinion are the most reliable, especially in the region of the saturated state of a system. Knowing the activity coefficient, we can calculate the fugacity by Eq. (5.1).

Fig. 14
Fugacity coefficients for selected liquids and gases at $Z_{cr} = 0.27$

Example 116. Calculate the fugacity of isobutane at 373.2 K and pressures of 10, 25, and 80 atm if $T_{cr} = 408$ K, $p_{cr} = 36$ atm, and $Z_{cr} = 0.289$.

Solution. We calculate the reduced parameters:

$$\tau = \frac{373.2}{408} = 0.915, \quad \pi_{10} = \frac{10}{36} = 0.278, \quad \pi_{25} = \frac{25}{36} = 0.695,$$

and $\pi_{80} = \dfrac{80}{36} = 2.22$

From Fig. 11 we find $\gamma_{10} = 0.88$, $\gamma_{25} = 0.66$, and $\gamma_{80} = 0.29$. The fugacities are:

$$f_{10} = 10 \times 0.88 = 8.8 \text{ atm}, \quad f_{25} = 25 \times 0.66 = 16.5 \text{ atm},$$
$$\text{and} \quad f_{80} = 80 \times 0.29 = 28.2 \text{ atm}$$

A comparison of the fugacities calculated using the activity coefficient with the values found by the graphical method shows that the deviation averages 8%.

We find the activity coefficients from Tables d and e of Appendix 19. We write out the values of γ for τ and π which are the closest
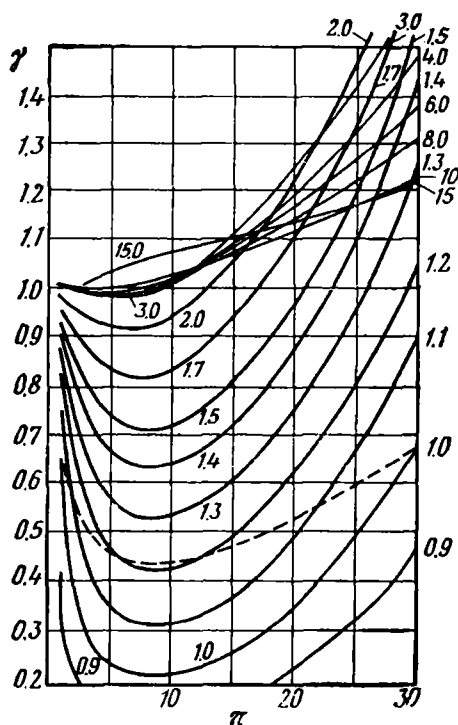
Fig. 15
Fugacity coefficients for selected liquids and gases at $Z_{cr} = 0.27$
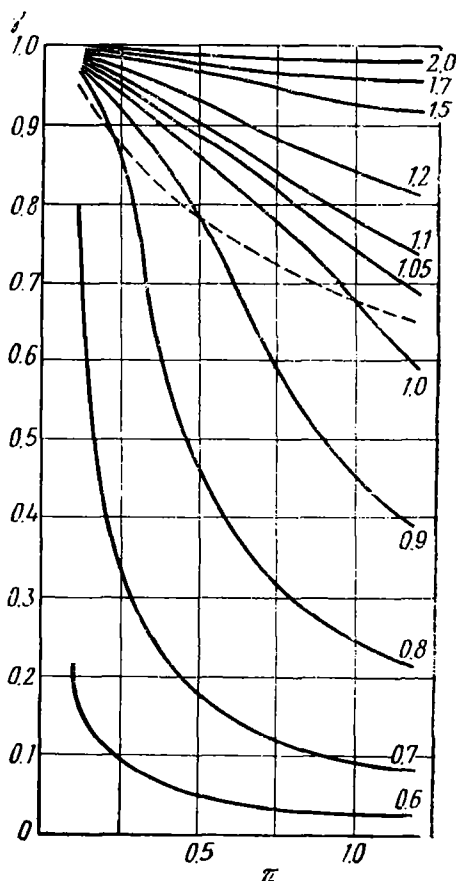
Fig. 16
Fugacity coefficients for selected liquids and gases at $Z_{cr} = 0.29$

to our calculated values of τ and π and conduct linear interpolation first for τ, and then for π (see the table on page 214). At $\pi > 1.8$, the value of Z_{cr} does not affect the values of γ.

The fugacities equal, respectively (in atm),

$$f_{10} = 10 \times 0.905 = 9.05, \quad f_{25} = 25 \times 0.638 = 15.9,$$

$$\text{and} \quad f_{80} = 80 \times 0.248 = 19.8$$

π	τ		
	0.9	1.0	0.915
0.2	0.936	0.953	0.939
0.3	0.888	0.920	0.893
0.278			0.905
0.6	0.697	0.821	0.715
0.7	0.608	0.790	0.634
0.695			0.638
2.0	0.236	0.396	0.261
3.0	0.181	0.306	0.200
2.22			0.248

A comparison of the calculated fugacities with the values found by the graphical method shows a good convergence of the values for pressures of 10 and 80 atm (a discrepancy of 4.0 to 8%), and lowering of the value by 10% for 25 atm.

The numerical values of γ which we have taken for $\pi = 0.6$ to 0.7 relate to the liquid state (under the dotted line in Table d of Appendix 19), while according to the graphical method the value of the real volume corresponds to the gaseous state. Consequently, γ should be taken for the state of a saturated vapour. At $\pi = 0.695$ we have $\gamma_{sat} = 0.740$ and $f = 18.6$ atm which gives an error of 5.7%.

Example 117. Calculate the fugacity of hydrogen at 500 K and $p = 250$ atm if $T_{cr} = 33.3$ K, $p_{cr} = 12.8$ atm, and $Z_{cr} = 0.29$.
Solution.

$$\pi = \frac{250}{12.8+8} = 12.02 \quad \text{and} \quad \tau = \frac{500}{33.3+8} = 12.6$$

From Fig. 11 we have $\gamma = 1.1$ and $f = 1.1 \times 250 = 275$ atm.

Example 118. Calculate the fugacity of ammonia at 500 K and $p = 50$ atm if $T_{cr} = 405.6$ K, $p_{cr} = 112.5$ atm, and $Z_{cr} = 0.242$.
Solution.

$$\pi = \frac{50}{112.5} = 0.445 \quad \text{and} \quad \tau = \frac{500}{405.6} = 1.112$$

From Table b of Appendix 19 for $Z_{cr} = 0.25$, we write out the activity coefficients for π and τ closest to the values we have calculated, and perform interpolation:

π	τ		
	1.1	1.2	1.12
0.4	0.913	0.936	—
0.5	0.888	0.918	—
0.445	0.903	0.928	0.908

We get $f = 0.908 \times 50 = 45.4$ atm.

5.1.5. Calculations Through the Compression Factor. In Eq. (5.7),
the volume correction α for a real gas is expressed through the com·
pression factor $Z = pV/RT$ (where V is the real volume of the
system at the pressure p). By Eq. (5.6)

$$\alpha = V_{\text{id}} - V = \frac{RT}{p} - \frac{ZRT}{p} = RT\left(\frac{1-Z}{p}\right) \tag{5.11}$$

Using Eq. (5.11) in (5.7), we get

$$\ln f = \ln p - \int_0^p (1 - Z)\, d\ln p \tag{5.12}$$

The integral in Eq. (5.12) is determined by graphical integration
over the area under the curve $(1 - Z) = \varphi(\ln p)$. The factor Z
is a function of the reduced parameters π, τ, and Z_{cr}. This functional
relationship is given in the form of graphs. It is tabulated in Ap-
pendix 20 [61]. Since $Z = \varphi(\pi, \tau)$, the reduced pressure is introduced
into the integral in Eq. (5.12). Hence when $\tau = \text{const}$, we get

$$\ln f = \ln p - \int_0^\pi (1 - Z)\, d\ln \pi \tag{5.13}$$

The integral in Eq. (5.13) is determined over the area under the
curve $(1 - Z) = \varphi(\ln \pi)$ for the pressure interval from 0 to π.
Equation (5.13) is used for calculating the activity coefficients.
Their values given in Appendix 19 have been calculated by this
method according to the compression factors determined by
L. Nelson.

Example 119. Use Eq. (5.13) to calculate the fugacity of isobutane
at 373.2 K and a pressure of 10, 25, and 80 atm if $T_{\text{cr}} = 408$ K,
$p_{\text{cr}} = 36$ atm, and $Z_{\text{cr}} = 0.289$.
Solution. We calculate the reduced pressures for the interval from 1
to 80 atm. We use the data in [61] to find the values of Z for $\tau =$
$= 373.2/408 = 0.915$ and enter the results obtained in a table,

in which we also fill in the relevant values of $1 - Z$ and $\log \pi$.

p	π	Z	$1 - Z$	$\log \pi$
1	0.0278	0.987	0.013	—1.556
3	0.0835	0.962	0.038	—1.078
5	0.139	0.930	0.070	—0.857
10	0.278	0.854	0.146	—0.556
15	0.417	0.775	0.225	—0.38
20	0.556	0.683	0.317	—0.255
25	0.695	0.596*	0.404	—0.158
30	0.835	0.511*	0.489	—0.088
40	1.11	0.188	0.812	0.045
50	1.39	0.205	0.795	0.143
60	1.66	0.241	0.759	0.22
80	2.22	0.323	0.677	0.347

* These values of Z have been taken for the saturated vapour.

We use the data of the table to plot a graph of $1 - Z$ against $\log \pi$ (see Fig. 17). Cross-hatched area *1* under the curve corresponds to $\int_{0}^{0.278} (1-Z)\, d \ln \pi$ and equals 0.0594. The negative sign of
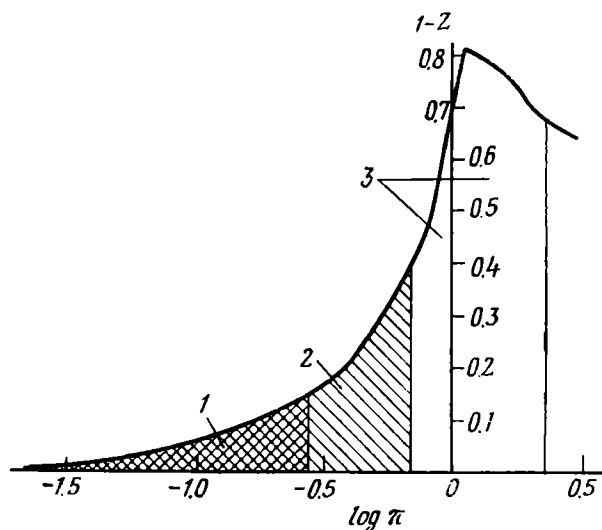
Fig. 17
Graph of $1 - Z$ against $\log \pi$ for isobutane at 373.2 K

log π in calculating the area is not taken into account because a negative area should be obtained only when the sign of $(1 - Z)$ changes.

According to Eq. (5.13), we have

$$\log f_{10} = \log 10 - 0.0594 - 0.9406 \quad \text{and} \quad f_{10} = 8.72 \text{ atm}$$

The integral $\int_{0}^{0.695} (1 - Z)\, d \ln \pi$ equals the sum of cross-hatched area *1* and hatched area *2*, i.e. 0.1628. Hence,

$$\log f_{25} = \log 25 - 0.1628 = 1.2351 \quad \text{and} \quad f_{25} = 17.18 \text{ atm}$$

Finally, the sum of areas *1*, *2*, and *3* equals 0.5305, whence,

$$\log f_{80} = \log 80 - 0.5305 = 1.3726 \quad \text{and} \quad f_{80} = 23.6 \text{ atm}$$

The fugacities calculated by the graphical method through the compression factors differ from those found according to experimental data (using the first graphical method) by from 2 to 10%.

Thus, a comparison of the fugacities calculated by different methods shows that the most reliable results are obtained through the activity coefficients and the compression factors.

5.2
Calculating the Composition of an Equilibrium Mixture in a Real System

When calculating the composition of an equilibrium mixture for reactions at high pressures, the partial fugacities should be used instead of the partial pressures in the equation of the law of mass action. For example for the reaction

$$A + 2B \rightleftarrows C + D$$
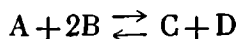
in the gaseous phase at a high pressure, the law of mass action has the form

$$K_f = \frac{f_C f_D}{f_A f_B^2} \tag{5.14}$$

where K_f = equilibrium constant of the reaction, which depends only on the temperature

f_A, f_B, f_C, and f_D = partial fugacities of the components of the system.

The partial fugacity is proportional to the fugacity of a given component:

$$f_i = x_i f_{0i}$$

where f_{0i} = fugacity of the i-th component in the pure form

x_i = mole fraction of the i-th component.

The fugacity is related to the total pressure of a system:

$$f_{0i} = \gamma_i p$$

where γ_i is the activity coefficient of the i-th component. Thus,

$$f_i = x_i \gamma_i p \tag{5.15}$$

After introducing Eq. (5.15) into (5.14), we get

$$K_f = \frac{\gamma_C x_C p \gamma_D x_D p}{\gamma_A x_A p (\gamma_B x_B p)^2} = \frac{\gamma_C \gamma_D}{\gamma_A (\gamma_B)^2} \frac{x_C x_D}{x_A x_B^2 p}$$

The second fraction in the right-hand side equals K_p while the first fraction will be designated by K_γ:

$$K_f = K_\gamma K_p, \quad \text{or} \quad K_p = \frac{K_f}{K_\gamma} \tag{5.16}$$

The quantity K_f, which is a function only of temperature, can be determined by using any of the methods described in Chap. 3 for calculating K_p for an ideal system. It is simple to calculate K_γ through the found values of the activity coefficients.

Example 120. Calculate the composition of the equilibrium mixture in the reaction of synthesis of methyl alcohol from CO and H_2 at 350 atm and 600 K if $(\Delta G^\circ_{600})_{form} = -28.52$ kcal/mol for the alcohol and $(\Delta G^\circ_{600})_{form} = -39.36$ kcal/mol for the CO [56]. The critical parameters of the components of the system are as follows:

	CH_3OH	CO	H_2
p_{cr}, atm	78.7	35.0	12.8
T_{cr}, K	513	134.1	32.2
Z_{cr}	0.22	0.29	0.29

Solution. The reaction is

$$CO + 2H_2 \rightleftarrows CH_3OH$$
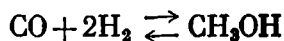
We use Eq. (3.2) to calculate the equilibrium constant of the reaction:

$$\log K_f = -\frac{-28.52 - (-39.36) \times 10^{-3}}{4.576 \times 600} = -3.949$$

and $K_f = 0.000\,1125$

We calculate the reduced parameters and determine the activity coefficients:

	CH_3OH	CO	H_2
π	$\dfrac{350}{78.7}=4{\cdot}45$	$\dfrac{350}{35}=10$	$\dfrac{350}{12.8+8}=16.8$
τ	$\dfrac{600}{513}=1.17$	$\dfrac{600}{134.1}=4.47$	$\dfrac{600}{32.2+8}=14.92$
γ_i	0.4435	1.02	1.121

We determine the activity coefficients according to Appendix 19, interpolating within the relevant interval of the values of π and τ. Next we find K_γ:

$$K_\gamma = \frac{\gamma_{alc}}{\gamma_{c.m}\gamma_{hyd}^2} = \frac{0.4435}{1.02 \times 1.121^2} = 0.35$$

where the subscripts "alc", "c.m", and "hyd" stand for CH_3OH, CO, and H_2, respectively, and by Eq. (5.16), we have

$$K_p = \frac{K_f}{K_\gamma} = \frac{0.000\,112\,5}{0.35} = 0.000\,32$$

The expression for K_p for the reaction is

$$K_p = \frac{x_{alc}p}{x_{c.m}p\,(x_{hyd}p)^2} = \frac{x_{alc}}{x_{c.m}\,(x_{hyd}p)^2}$$

For the equilibrium system we have:

$$CO + 2H_2 \rightleftarrows CH_3OH$$

$$n_i \quad \ldots \ldots \quad 1-y \quad 2(1-y) \quad y \quad \sum n = 3-2y$$

Hence,

$$x_{alc} = \frac{y}{3-2y}, \quad x_{c.m} = \frac{1-y}{3-2y}, \quad x_{hyd} = \frac{2(1-y)}{3-2y},$$

and $\quad K_p = \dfrac{y\,(3-2y)^2}{4\,(1-y)^3\,p^2}$

The reaction corresponds to the 12th class of reactions (Appendix 18), whence,

$$\log K_p + 2\log p = \log M$$

Since $\log K_p = \log 0.000\,32 = -3.495$, and $\log p = \log 350 = 2.544$, we get

$$\log M = -3.495 + 5.088 = 1.593$$

and interpolation in Appendix 18 gives $y = 0.792$. Hence,

$$x_{alc} = 0.56, \quad x_{c.m} = 0.146, \quad \text{and} \quad x_{hyd} = 0.292$$

5.3

Empirical Methods
for Calculating the Critical Parameters

Several empirical relationships have been proposed that permit us to calculate the critical parameters with different degrees of reliability. R. Reid and T. Sherwood [61] analysed different methods proposed for calculating the critical temperatures and pressures and recommend Lydersen's method and that of J. Forman and G. Thodos as the most reliable ones.

Lydersen's Method. This method should be considered as a modification of Guldberg's rule:

$$T_{cr} = \frac{T_{n.\,b.\,p}}{\theta} \qquad (5.17)$$

where $T_{n.b.p}$ = normal boiling point in kelvins (at $p = 1$ atm)
  θ = constant parameter for each compound.
The value of θ is determined by the equation

$$\theta = 0.567 + \sum \Delta_T - \left(\sum \Delta_T\right)^2 \qquad (5.18)$$

where $\sum \Delta_T$ is the sum of structural and atomic constants for the groups into which the compound being considered can be divided (their values are given in Appendix 21).

The following equation is proposed for calculating the critical pressures:

$$p_{cr} = \frac{M}{(\Phi + 0.34)^2} \qquad (5.19)$$

where M = molecular weight of the compound
  Φ = constant determined by summation of Δ_p—structural and atomic constants (their values are given in Appendix 21).

Forman and Thodos Method. This method permits us to calculate the critical parameters through the constants of the van der Waals equation as follows:

$$T_{cr} = \frac{8a}{27bR} \qquad (5.20)$$

$$p_{cr} = \frac{a}{27b^2} \qquad (5.21)$$

where R = molar gas constant, equal to 82.06 cm^3·atm/mol·K
a and b = constants of the van der Waals equation, in cm^6/mol^2·atm and cm^3/mol, respectively.

This method makes it possible to calculate the constants a and b for compounds whose properties do not obey the van der Waals equa-

tion. The main advantage of the method is that it does not require a knowledge of any physical constants of a compound that are determined experimentally and allows us to calculate the critical parameters with account taken of the branching nature of a molecule of the compound.

The method is based on the following postulates. A molecule is divided into a total number of n units, equal to the number of carbon atoms and functional groups. For example for C_2H_5Br we have $n = 3$. for C_4H_9OH we have $n = 5$, etc. The tables in Appendix 22 give the group contributions $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for different kinds of hydrocarbons and the contributions for the presence of double and triple bonds in a compound. The coefficients of the van der Waals equation are calculated by summation of all the contributions

$$a = \left(\sum \Delta a^{2/3}\right)^{3/2} \quad \text{and} \quad b = \left(\sum \Delta b^{3/4}\right)^{4/3}$$

The following type numbers are assigned to the carbon atoms in hydrocarbons:

aliphatic hydrocarbons	$-CH_3$	$>CH_2$	$-CH$	$>C<$
	1	2	3	4

dienes	$=CH$
	3_u

naphthenes	$-CH_2-$	$>CH-$	$>C<$
	2_n	3_n	4_n

aromatic hydrocarbons	$=CH$	$=C<$	$C=C<$
	3_a^i	4_a	4_p
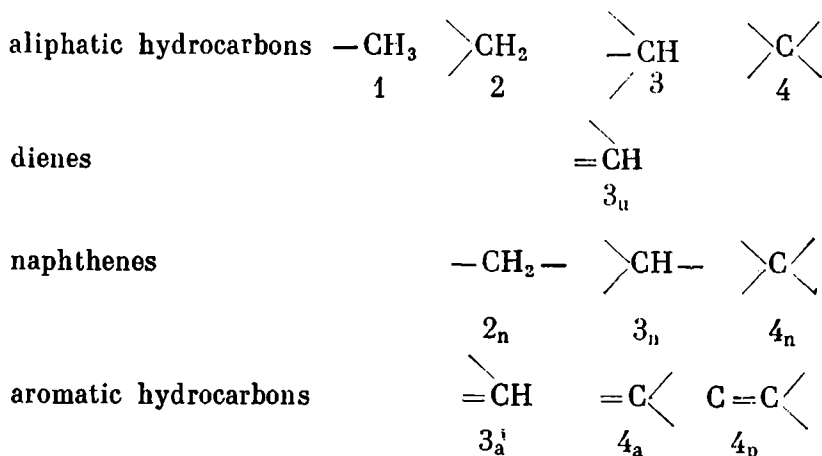
The last kind of structural group 4_p relates to aromatic compounds with fused (condensed) rings.

The contributions for functional groups are calculated by the equations

$$\Delta a^{2/3} = \frac{q}{n} + k \quad \text{and} \quad \Delta b^{3/4} = \frac{s}{n} + t$$

where n = total number of structural groups in the compound (carbon atoms and functional atoms)

q, k, s, t = constants whose values for the corresponding functional groups are given in Appendix 22.

The sum of the contributions for naphthene and aromatic compounds takes into account the formation of rings and branchings.

The values of $\sum \Delta a^{2/3}$ and $\sum \Delta b^{3/4}$ for unsaturated compounds are determined in the following sequence:

(a) the sum of the contributions for the aliphatic compound having the same carbon skeleton is found;

(b) the first double bond is inserted, the type number of the carbon atom being taken according to the aliphatic compound, and the appropriate contribution is added;

(c) the second double bond is inserted and the relevant contribution is added. In determining the type number of the carbon atom for inserting the second double bond, the presence in the compound of the first double bond is taken into account. For example for a compound having one double bond of the kind $C\overset{\beta}{-}C\overset{\alpha}{-}C=C\overset{\gamma}{-}C\overset{\delta}{-}C\overset{\varepsilon}{-}C$,
$$\underset{C}{\big|}$$
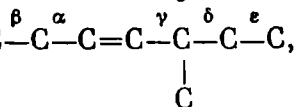
the introduction of the second bond in the α position corresponds to the contribution 3_u-2, in the β position to the contribution $3_u \leftarrow$ $\leftarrow$ 2-1, in the γ position to the contribution 3_u-3, in the δ position to the contribution 3-2, and in the ε position to the contribution 2-1, i.e. it is taken according to the first double bond.

In calculating the critical parameters for halogen-containing compounds in which more than one halogen atom is attached to a single carbon atom, for instance $-C\overset{F}{\underset{Cl}{\diagdown}}Cl$, the lowest-atomic-weight halogen is considered first, then the next higher, etc., i.e. the first contribution is for fluorine, and the second and third are for chlorine.

A comparison of calculated critical parameters with those found in reliable experiments shows that Lydersen's method for most compounds gives an error up to 2%, except for alcohols heavier than butanol (the deviation for them reaches 5%). The critical parameters calculated by the Forman and Thodos method deviate from the experimentally found values by less than 1% for hydrocarbons and up to 2% for compounds containing functional groups.

Example 121. Calculate the critical parameters for 2,2,3-trimethylbutane according to the methods considered above, and compare the found values with the experimental ones: $T_{cr} = 531.5$ K, $p_{cr} = 29.7$ atm, and $T_{n.b.p} = 354$ K.

Solution. The compound 2,2,3-trimethylbutane has the structure
$$\begin{matrix} & & C & & \\ & & | & & \\ C & - & C & - & C & - & C. \end{matrix}$$
When calculating by Lydersen's method, we take
$$\begin{matrix} & | & | & \\ & C & C & \end{matrix}$$
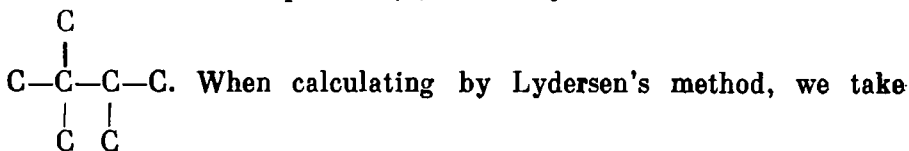
the values of Δ_T and Δ_p from Appendix 21:

Group	Number of groups	Δ_T	Δ_p
$-CH_3$	5	$0.02 \times 5 = 0.10$	$0.227 \times 5 = 1.135$
$>C<$	1	0.0	0.21
$>CH$	1	0.012	0.21
		0.112	1.555

By Eq. (5.18) we have

$$\theta = 0.567 + 0.112 - (0.112)^2 = 0.667$$

We calculate T_{cr} by Eq. (5.17):

$$T_{cr} = \frac{354}{0.667} = 530.7 \text{K}$$

We calculate the error of the found value in comparison with the experimental one:

$$\frac{531.5 - 530.7}{531.5} \times 100 = 0.15\%$$

We find p_{cr} by Eq. (5.19):

$$p_{cr} = \frac{100}{(1.555 + 0.34)^2} = 27.9 \text{ atm}$$

The error is 6%.

Now we use the Forman and Thodos method for our calculations. For the given compound $n = 7$. We use Appendix 22 to find the contributions for the corresponding type of carbon atom at $n = 7$:

Type of carbon atom	Number of groups	$\Delta a^{2/3}$	$\Delta b^{3/4}$
1, i.e. $-CH_3$	5	$14\,803 \times 5$	11.453×5
3, i.e. $>CH$	1	9 614	-0.460
4, i.e. $>C<$	1	4 123	-7.909
		87 752	48.896

Hence, $a = (87\ 752)^{3/2} = 25.99 \times 10^6,$ and $b = (48.896)^{4/3} =$ $= 178.7$.

We calculate T_{cr} by Eq. (5.20):

$$T_{cr} = \frac{8 \times 25.99 \times 10^6}{27 \times 178.7 \times 82.06} = 525.2\ K$$

The error of the calculated value is 1.2%.
We find p_{cr} by Eq. (5.21):

$$p_{cr} = \frac{25.99 \times 10^6}{27 \times 178.7^2} = 30.1\ atm$$

The error is 1.35%.

Example 122. Calculate the critical parameters of *m*-xylene. Their experimentally found values are $p_{cr} = 36.0$ atm, $T_{cr} = 618$ K, and $T_{n.b.p} = 412.2$ K.

Solution. We use Lydersen's method for the calculations. We take the contributions for the groups from Appendix 21:

Group	Number of groups	Δ_T	Δ_p
$-CH_3$	2	0.020×2	0.227×2
$=CH$ (ring)	4	0.011×4	0.154×4
$= C\Big\langle$ (ring)	2	0.011×2	0.154×2
		0.106	1.378

By Eq. (5.18) we have

$$\theta = 0.567 + 0.106 - (0.106)^2 = 0.662$$

By Eq. (5.17)

$$T_{cr} = \frac{412.2}{0.662} = 622.6\ K$$

The error is 0.74%.
The molecular mass of *m*-xylene is 106. Consequently, by Eq. (5.19), we have

$$p_{cr} = \frac{106}{(1.378 + 0.34)^2} = 35.9\ atm$$

The error is 0.28%.

We use the Forman and Thodos method for calculations. The number of structural groups is $n = 8$. We take the contributions for the given kinds of structural groups from Appendix 22:

Type of carbon atom	Number of groups	$\Delta a^{2/3}$	$\Delta b^{3/4}$
1, i.e. $-CH_3$	2	$14\,764 \times 2$	11.453×2
3_a, i.e. $=CH$	4	$11\,646 \times 4$	5.991×4
4_a, i.e. $=C<$	2	$11\,144 \times 2$	1.042×2
Branching in aromatic ring 1-3		$-1\,597$	-0.806
		$96\,803$	48.14

Hence, $a = (96\,803)^{3/2} = 30.11 \times 10^6$, and $b = (48.14)^{4/3} = 175.1$.

$$T_{cr} = \frac{8 \times 30.11 \times 10^6}{27 \times 175.1 \times 82.06} = 621 \text{ K}$$

The error is 0.48%.

$$p_{cr} = \frac{30.11 \times 10^6}{27\,(175.1)^2} = 36.3 \text{ atm}$$

The error is 0.83%.

Example 123. Calculate the critical parameters of triethylamine using the Forman and Thodos method and compare them with the experimentally found values of $T_{cr} = 532$ K and $p_{cr} = 30$ atm.
Solution. The structure is $C_2H_5-N-C_2H_5$, and the number of
$$\underset{C_2H_5}{\overset{|}{}}$$
structural groups is $n = 7$. In Appendix 22 we find the group contributions and constants for calculating the contributions for a tertiary amine:

$$\Delta a^{2/3} = \frac{q}{n} + k = \frac{60\,200}{7} - 4300 = 4300$$

$$\Delta b^{3/4} = \frac{s}{n} + t = \frac{29.2}{7} - 7.90 = -3.73$$

Type of carbon atom or group	Number of groups	$\Delta a^{2/3}$	$\Delta b^{3/4}$
1, i.e. $-CH_3$	3	$14\,803 \times 3$	11.453×3
2, i.e. $\diagdown CH_2$ $\diagup$	3	$13\,678 \times 3$	6.262×3
$-N\diagdown$	1	$4\,300$	-3.73
		$89\,743$	49.415

$$a = (89\,743)^{3/2} = 26.52 \times 10^6 \quad \text{and} \quad b = (49.415)^{4/3} = 181.3$$

$$T_{cr} = \frac{8 \times 26.52 \times 10^6}{27 \times 181.3 \times 82.06} = 529.5 \text{ K}$$

The error is 0.47%.

$$p_{cr} = \frac{26.52 \times 10^6}{27\,(181.3)^2} = 29.9 \text{ atm}$$

The error is 0.3%.

Example 124. Calculate the critical parameters of isoamyl formate; $T_{n.b.p} = 396.7$ K.

Solution. The structure of the compound is $CH_3-CH-CH_2-$
$$\underset{\displaystyle CH_3}{|}$$

$-CH_2-O-C=O.$
$$\underset{\displaystyle H}{|}$$

We use the Forman and Thodos method for calculations. The total number of structural groups in the compound is $n = 6$. In Appendix 22 we find the constants of the equation for calculating the contribution of the ester group:

$$\Delta a^{2/3} = \frac{35\,140}{6} + 26\,800 = 32\,657 \quad \text{and} \quad \Delta b^{3/4} = \frac{2.29}{6} +$$

$$+ 15.80 = 16.182$$

From the same Appendix we write out the contributions for the hydrocarbon groups:

Type of carbon atom or group	Number of groups	$\Delta a^{2/3}$	$\Delta b^{3/4}$
1, i.e. $-CH_3$	2	$14\,854\times2$	11.453×2
2, i.e. $>CH_2$	2	$13\,678\times2$	6.262×2
3, i.e. $-CH<$	1	$10\,270$	0.101
$-O-C=O$ $\quad\vert$ $\quad H$	1	$32\,657$	16.182
		$99\,991$	51.713

$$a = (99\,991)^{3/2} = 31.6 \times 10^6 \quad \text{and} \quad b = (51.713)^{4/3} = 192.6$$

$$T_{cr} = \frac{8 \times 31.6 \times 10^6}{27 \times 192.6 \times 82.06} = 594 \text{ K} \quad \text{and} \quad p_{cr} = \frac{31.6 \times 10^6}{27\,(192.6)^2} =$$

$$= 36.5 \text{ atm}$$

We use Lydersen's method for calculations. We take the structural and atomic contributions from Appendix 21:

Group	Number of groups	Δ_T	Δ_p
$-CH_3$	2	0.020×2	0.227×2
$>CH_2$	2	0.020×2	0.227×2
$>CH-$	1	0.012	0.210
$-COO-$ (ester)	1	0.047	0.47
		0.139	1.588

$$\theta = 0.567 + 0.139 - (0.139)^2 = 0.687$$

$$T_{cr} = \frac{396.7}{0.687} = 578 \text{ K} \quad \text{and} \quad p_{cr} = \frac{116}{(1.588+0.34)^2} = 31.2 \text{ atm}$$

(The molecular weight of isoamyl formate is 116.)

5.4

Calculation of Enthalpies of Substances and Heats of Reactions Conducted at High Pressures

Let us find the pressure dependence of the enthalpy at constant temperature. For this purpose, we differentiate the basic equation of the enthalpy $H = U + pV$ with respect to pressure at $T = $ const:

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T + V + p\left(\frac{\partial V}{\partial p}\right)_T$$

Since $\left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T$, then

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{5.22}$$

Integration of Eq. (5.22) within the limits from 1 to p atm at $T = $ const allows us to determine the absolute enthalpy of a substance:

$$H_{p,\,T} = H_{p=1,\,T} + \int_1^p V\,dp - T\int_1^p \left(\frac{\partial V}{\partial T}\right)_p dp \tag{5.23}$$

The heat of a reaction equals the change in the enthalpy of a system. Therefore,

$$\Delta H_{p,\,T} = \Delta H_T^\circ + \int_1^p \Delta V\,dp - T\int_1^p \left(\frac{\partial \Delta V}{\partial T}\right)_p dp \tag{5.24}$$

where $\Delta H_T^\circ = $ heat of a reaction in the standard state
$\Delta V = $ change in the volume of the system as a result of the reaction.

The heat of a reaction at any pressure may be calculated by Eq. (5.24) if experimental data permit us to determine the integrals of the equation. A different method is resorted to in practice, however.

The compression factor is introduced into Eq. (5.22): since

$$Z = \frac{pV}{RT} \quad \text{and} \quad \left(\frac{\partial Z}{\partial T}\right)_p = -\frac{pV}{RT^2} + \frac{p}{RT}\left(\frac{\partial V}{\partial T}\right)_p =$$

$$= -\frac{p}{RT^2}\left\{V - T\left(\frac{\partial V}{\partial T}\right)_p\right\}$$

then

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{RT^2}{p}\left(\frac{\partial Z}{\partial T}\right)_p \tag{5.25}$$

Expressing the pressure and temperature in Eq. (5.25) through the reduced parameters, we get

$$\left(\frac{\partial H}{\partial \pi}\right)_{\tau} = -\frac{R\tau^2 T_{cr}}{\pi}\left(\frac{\partial Z}{\partial \tau}\right)_{\pi}$$

As a result of integrating the last equation within the interval from the standard state to a state at any pressure, we have

$$\frac{H-H^\circ}{T_{cr}} = -R\tau^2 \int_0^{\pi}\left(\frac{\partial Z}{\partial \tau}\right)_{\pi} d\ln \pi \qquad (5.26)$$

The solution of Eq. (5.26) is given in the form of graphs (Figs. 18 and 19) plotted by R. Kordbachen and Chi Tien, where $(H^\circ - H)/T_{cr} = \varphi(\pi, \tau)$, or in the form of tables compiled by A. Lydersen and O. Hougen (Appendix 23), where the values of $(H^\circ - H)/T_{cr}$ are given as a function of π, τ, and Z_{cr}. R. Reid and T. Sherwood [61] suggest that for substances for which Z_{cr} is close to 0.27 and which are in the state of a saturated vapour reliable values of the change in enthalpy with pressure are obtained both when graphs and tables are used. If, however, the state of a substance is close to the saturated one or if the value of Z_{cr} for it considerably differs from 0.27, it is more reliable to use tables (Appendix 23). Generally the maximum error is obtained for low reduced pressures, its value reaching 10%.
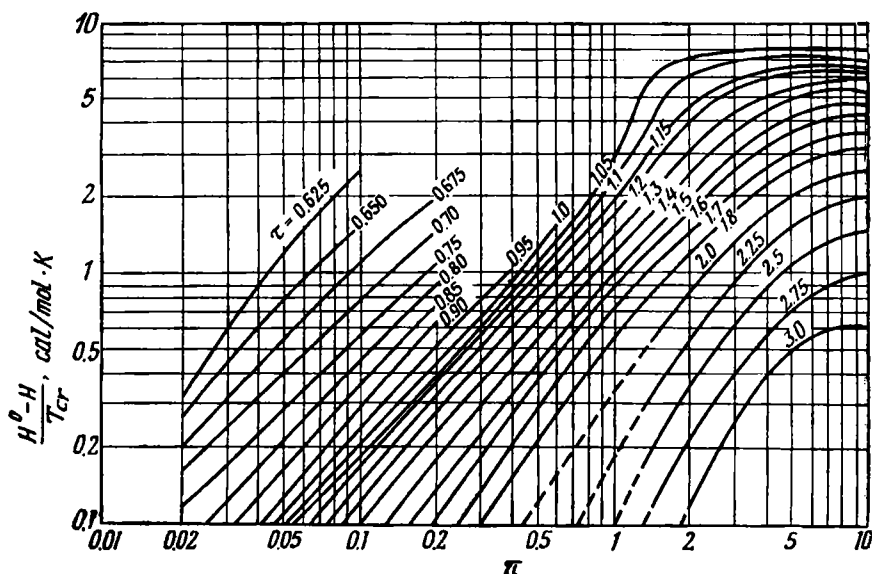
Fig. 18
Dependence of enthalpy on reduced temperature and pressure [61]
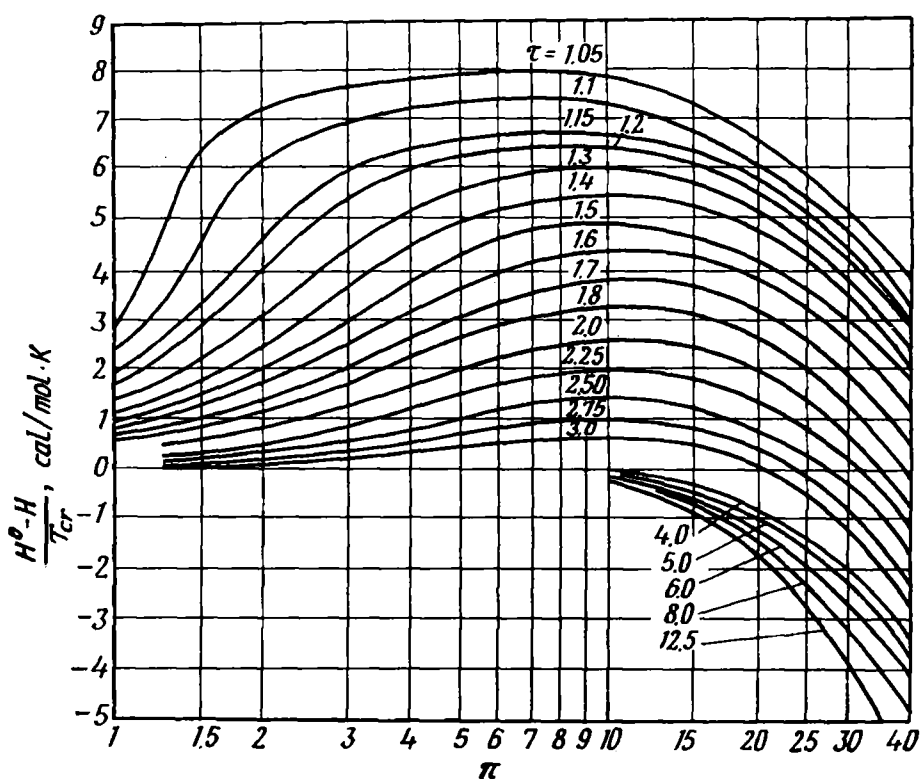
Fig. 19
Dependence of enthalpy on reduced temperature and pressure [61]

The heat of a reaction conducted at high pressures is determined as follows. We find the change in the enthalpy $(H° - H)/T_{cr} = \varphi(\pi, \tau, Z_{cr})$ for each reagent at the given reduced parameters according to a graph (see Figs. 18 and 19) or tables (Appendix 23). Next we calculate the standard heat of the reaction at the given temperature, and then the heat of the reaction for the given conditions:

$$\Delta H_{p,\,T} = \Delta \left[\left(\frac{H - H°}{T_{cr}} \right) T_{cr} \right] + \Delta H_T° \tag{5.27}$$

where

$$\Delta \left[\left(\frac{H - H°}{T_{cr}} \right) T_{cr} \right] = \sum \left[\left(\frac{H - H°}{T_{cr}} \right) T_{cr} \right]_{pr} - \left[\left(\frac{H - H°}{T_{cr}} \right) T_{cr} \right]_{r}$$

Example 125. Calculate the heat of the reaction of hydrogenation of toluene at 650 K and 150 atm.

Solution. The equation of the reaction is

$$C_6H_5CH_3(g) + 3H_2 \rightarrow C_6H_{11}CH_3(g)$$

The standard heats of formation of the substances from simple compounds at 650 K, taken from [9], and the critical parameters (Appendix 1) are given below:

	$C_6H_5CH_3$	H_2	$C_6H_{11}CH_3$
$(\Delta H^\circ_{650})_{form}$, kcal/mol	7.500	0	—43.98
p_{cr}, atm	41.6	12.8	34.3
T_{cr}, K	592	33.3	572
Z_{cr}	0.27	0.29	0.25

The standard heat of the reaction at 650 K is

$$\Delta H^\circ_{650} = -43.98 - 7.5 = -51.48 \text{ kcal}$$

The reduced parameters are:

For $C_6H_5CH_3$: $\quad \tau = \dfrac{650}{592} = 1.1 \quad$ and $\quad \pi = \dfrac{150}{41.6} = 3.60$

For H_2: $\quad \tau = \dfrac{650}{33.3+8} = 15.74 \quad$ and $\quad \pi = \dfrac{150}{12.8+8} = 7.21$

For $C_6H_{11}CH_3$: $\quad \tau = \dfrac{650}{572} = 1.13 \quad$ and $\quad \pi = \dfrac{150}{34.3} = 4.37$

In Appendix 23, we find for each substance the value of $(H^\circ - H)/T_{cr}$, interpolating where necessary, and calculate the difference $(H - H^\circ)$ for each reagent:

	$C_6H_5CH_3$	H_2	$C_6H_{11}CH_3$
$(H^\circ - H)/T_{cr}$, cal/mol·K	7.38	0.152	7.24
$\left(\dfrac{H - H^\circ}{T_{cr}}\right) T_{cr} = H - H^\circ$, cal	—4369	—5	—4141

For the reaction, we have

$$\Delta (H - H^\circ) = -4141 - (-4369 - 5 \times 3) = 243 \text{ cal}$$

$$\Delta H^{150}_{650} = 243 - 51\,480 = -51\,237 \text{ cal}$$

The results of our calculations show that the change in the heat of the reaction of hydrogenation with pressure is 0.5 % of the standard value, i.e. is within the limits of the accuracy of determining the standard heats of formation of substances. Therefore, such a correction may not be introduced in practical calculations.

Example 126. Calculate the enthalpy of *n*-butane at 500 K and 100 atm relative to the ideal gaseous state at 0 K; $T_{cr} = 425.2$ K, $p_{cr} = 37.5$ atm, and $Z_{cr} = 0.274$.

Solution. The reduced parameters are $\pi = 100/37.5 = 2.67$ and $\tau = 500/425.2 = 1.17$. At such parameters, the n-butane will be in the state of a superheated vapour. Therefore, we determine the ratio $(H^\circ - H)/T_{cr}$ from Fig. 18; it equals 5.5. The enthalpy relative to the standard enthalpy at 500 K is

$$H - H^\circ = -5.5 \times 425.2 = -2338 \text{ cal/mol}$$

In [9] we find the ratio $(H^\circ - H_0^\circ)/T$ for n-butane; it equals 21.19. Hence,

$$H^\circ - H_0^\circ = 21.19 \times 500 = 10\ 595 \text{ cal/mol}$$

The required quantity is

$$(H_{500}^{100} - H_0^\circ) = (H - H^\circ) + (H^\circ - H_0^\circ) =$$
$$= -2338 + 10\ 595 = 8257 \text{ cal/mol}$$

Example 127. How will a change in the pressure in the system from 100 to 50 atm affect the heat of the reaction of hydrocracking of n-dodecane at 700 K? Take into consideration that the hydrocracking proceeds in the following directions:

(I) $n\text{-}C_{12}H_{26} + H_2 \rightarrow 2n\text{-}C_6H_{14}$

(II) $n\text{-}C_{12}H_{26} + 2H_2 \rightarrow 2n\text{-}C_5H_{12} + C_2H_6$

(III) $n\text{-}C_{12}H_{26} + 3H_2 \rightarrow 2n\text{-}C_4H_{10} + C_3H_8 + CH_4$
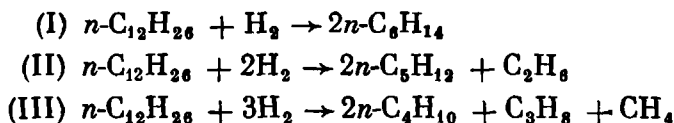
Solution. We tabulate all the data needed for the calculations, including the standard heats of formation of the substances according to [9], the critical parameters from Appendix 1, the calculated reduced parameters, and the values of $(H^\circ - H)/T_{cr}$ found according to Appendix 23.

z_{cr}	Compound	$(\Delta H_{700}^\circ)_{form},$ kcal/mol	$T_{cr},$ K	$p_{cr},$ atm	π_{100}	π_{50}	τ	$\left(\dfrac{H^\circ-H}{T_{cr}}\right)_{100}$	$\left(\dfrac{H^\circ-H}{T_{cr}}\right)_{50}$	$(H-H^\circ)_{100}$	$(H-H^\circ)_{50}$
0.238	$n\text{-}C_{12}H_{26}$	−82.48	659.2	17.9	5.6	2.8	1.06	8.42	7.74	−5550	−5102
0.292	H_2	0	33.3	12.8	4.8	2.4	16.95	0.106	0.04	−3.5	−1.3
0.264	$n\text{-}C_6H_{14}$	−47.36	507.9	29.9	3.35	1.67	1.38	4.00	2.1	−2029	−1065
0.269	$n\text{-}C_5H_{12}$	−41.48	469.8	33.3	2.96	1.48	1.49	2.88	1.44	−1352	−676
0.274	$n\text{-}C_4H_{10}$	−35.70	425.2	37.5	2.67	1.33	1.65	1.97	0.98	−838	−417
0.277	C_3H_8	−29.49	370.0	42.0	2.38	1.19	1.89	1.22	0.58	−452	−214
0.285	C_2H_6	−23.98	305.5	48.2	2.08	1.04	2.29	0.71	0.45	−216	−138
0.29	CH_4	−20.40	191.1	45.8	2.19	1.1	3.66	0.2	0.2	−38	−38

The heats of the reactions in standard conditions are:

(I) $\Delta H^\circ_{700} = -2 \times 47.36 + 82.48 = -12.24$ kcal $=$
$= -12\,240$ cal

(II) $\Delta H^\circ_{700} = -2 \times 41.48 - 23.98 + 82.48 =$
$= -24.46$ kcal $= -24\,460$ cal

(III) $\Delta H^\circ_{700} = -2 \times 35.70 - 29.49 - 20.40 + 82.48 =$
$= -38.81$ kcal $= -38.810$ cal

The changes in the enthalpies of the reactions at 100 atm are:

(I) $\Delta\,(H - H^\circ) = -2 \times 2029 + 5550 + 3.5 = 1495.5$ cal

(II) $\Delta\,(H - H^\circ) = -2 \times 1352 - 216 + 5550 + 2 \times 3.5 =$
$= 2637$ cal

(III) $\Delta\,(H - H^\circ) = -2 \times 838 - 452 - 38 + 5550 +$
$+ 3 \times 3.5 = 3391$ cal

The changes in the enthalpies of the reactions at 50 atm are:

(I) $\Delta\,(H - H^\circ) = -2 \times 1065 + 5102 + 1.3 = 2974$ cal

(II) $\Delta\,(H - H^\circ) = -2 \times 676 - 138 + 5102 + 2 \times 1.3 =$
$= 3615$ cal

(III) $\Delta\,(H - H^\circ) = -2 \times 417 - 214 - 38 + 5102 +$
$+ 3 \times 1.3 = 4020$ cal

The heats of the reactions at 100 atm are:

(I) $\Delta H^{100}_{700} = 1495.5 - 12\,240 = -10\,745$ cal

(II) $\Delta H^{100}_{700} = 2637 - 24\,460 = -21\,823$ cal

(III) $\Delta H^{100}_{700} = 3391 - 38\,810 = -35\,419$ cal

The heats of the reactions at 50 atm are:

(I) $\Delta H^{50}_{700} = 2974 - 12\,240 = -9266$ cal

(II) $\Delta H^{50}_{700} = 3615 - 24\,460 = -20\,845$ cal

(III) $\Delta H^{50}_{700} = 4020 - 38\,810 = -34\,790$ cal

A comparison of the calculated reaction heats shows that the change in pressure affects the heat of the reaction proceeding in the first direction to a greater extent than those of the other two reactions.

Problems

233. Calculate the fugacity of chlorine at 433.2 K, 50 and 95 atm using (a) the graphical method according to the volume correction; and (b) according to the activity coefficients. The critical parameters are $T_{cr} = 417.2$ K, $p_{cr} = 76.1$ atm, and $Z_{cr} = 0.276$. The molar volumes of chlorine at different pressures are as follows [66]:

p, atm . . .	1.02	2.04	5.44	10.2	20.4	27.0	34.0	54.5	76.0	95.2
V, cm³/mol	34 700	17 240	6 375	3 330	1 592	1 150	885	478	265	122

234. Calculate the fugacity of carbon monoxide according to all the methods considered above at 273.2 K, 100 and 500 atm, using the following experimental data [66]:

p, atm . . .	1	25	50	75	100	150	200	300	400	500	600
V, cm³/mol	22 401	884	437	290	217	147	114	84	70	62	57

The critical parameters are $T_{cr} = 134.4$ K, $p_{cr} = 34.6$ atm, and $Z_{cr} = 0.296$. The constants of the van der Waals equation are $a = 1.48$ dm⁶·atm/mol², and $b = 0.0399$ dm³/mol.

235. For ethylene, the experimentally determined molar volumes at different pressures and at 313.2 K have the following values [66]:

p, atm . . .	10	20	40	60	80	100	140	180	200
V, cm³/mol	2520	1195	520	284	159	108	85.5	77.5	75.1

p, atm . . .	250	300	400	500	600	700	800	900	1000
V, cm³/mol	71.0	65.5	62.5	61.4	59.3	57.9	56.5	55.3	54.5

Calculate the fugacity of ethylene at 250 and 1000 atm using the methods of calculation considered above. The critical parameters are $T_{cr} = 283$ K, $p_{cr} = 50.3$ atm, and $Z_{cr} = 0.27$. The constants of the van der Waals equation are $a = 4.47$ dm⁶·atm/mol², and $b = 0.057$ dm³/mol.

236. Calculate the fugacity of acetylene at 320 K and 100 atm if its density at this pressure is 0.3860 g/cm³. The critical parameters are $T_{cr} = 308.7$ K, $p_{cr} = 61.6$ atm, and $Z_{cr} = 0.274$. Compare the fugacities determined according to the approximate method and by using the activity coefficients.

237. Determine the fugacity of acetone at 420 K and 80 atm. The critical parameters are $T_{cr} = 508.7$ K, $p_{cr} = 46.6$ atm, and $Z_{cr} = 0.237$.

238. Calculate the fugacity of hydrogen at 100 and 1000 atm, and at $T = 198.2$ K, using (a) the graphical method according to the volume correction; (b) the approximate method; and (c) the activity coefficients. The critical parameters are $T_{cr} = 33.2$ K,

$p_{cr} = 12.8$ atm, and $Z_{cr} = 0.29$. The molar volumes of hydrogen at various pressures are as follows [66]:

p, atm . . .	25	50	75	100	150	200	300
V, cm³/mol	661.4	336.7	228.7	174.8	121.3	94.7	68.3

p, atm . . .	500	800	1000
V, cm³/mol	47.5	35.8	31.95

239. Find the fugacity of ethane at 473.2 K, 300 and 100 atm using all the methods considered above. The experimentally determined molar volumes are as follows [65]:

p, atm . . .	2	5	10	20	30	40	60	80
V, cm³/mol	19 950	7 940	3 940	1 940	1 270	939	610	444

p, atm . . .	100	160	200	300
V, cm³/mol	348	208	166.8	121.4

The critical parameters are $T_{cr} = 305.4$ K, $p_{cr} = 48.5$ atm, and $Z_{cr} = 0.285$. The constants of the van der Waals equation are $a = 2.66$ dm⁶·atm/mol², and $b = 0.043$ dm³/mol.

240. The molar volume of methane at 203.2 K and 60 atm is 125.4 cm³. Calculate the fugacity of methane in these conditions using the van der Waals equation, the approximate method, and also the activity coefficients. The critical parameters are $T_{cr} = 151.1$ K, $p_{cr} = 45.8$ atm, and $Z_{cr} = 0.29$. The constants of the van der Waals equation are $a = 2.26$ dm⁶·atm/mol², and $b = 0.043$ dm³/mol.

241. Calculate the fugacity of chlorotrifluoromethane (Freon 13) at 323.2 K and 50 atm, if $T_{cr} = 304$ K, $p_{cr} = 39$ atm, and $Z_{cr} = 0.277$.

242. The compression factor of toluene at 600 K has the following values depending on the pressure:

p, atm	1	4	10	20	30	40	50	75	95	110
Z . . .	0.99	0.962	0.914	0.804	0.701	0.424	0.242	0.291	0.345	0.39

Calculate the fugacity at 100 atm. Compare it with the value calculated by Eq. (5.1).

243. Determine the fugacity of steam at 700 K and 200 atm according to the known values of the compression factor:
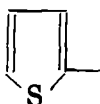
p, atm	10	20	50	75	100	130	150	180	200
Z . .	0.988	0.974	0.953	0.907	0.877	0.807	0.794	0.745	0.707

244. Calculate the critical parameters for the compounds tabulated below and determine the accuracy of the considered methods of calculation; the critical parameters according to [61] are given in the table for purposes of comparison.

Compound	$T_{n.b.p}$, K	T_{cr}, K	p_{cr}, atm
Acetonitrile CH_3CN	355.2	547.9	47.7
Diethyl sulphide $(C_2H_5)_2S$	365.0	557.0	39.1
Ethylpropyl ether $C_2H_5OC_3H_7$	334.6	500.6	32.1
Hydrogen sulphide H_2S	213.6	373.6	88.9
2,2,4-Trimethylpentane C_8H_{18}	372.4	544.3	25.5
Isopropylbenzene $C_6H_5CH(CH_3)_2$	425.6	635.9	32.0

245. Calculate the critical parameters of the following compounds: (1) hexahydrocumene $C_6H_{11}CH(CH_3)_2$ ($T_{n.b.p} = 427.8$ K); (2) perfluoroisobutene C_4F_8; (3) isoprene $CH_2=C(CH_3)-CH=CH_2$ ($T_{n.b.p} = 307.3$ K); (4) hydroquinone $C_6H_4(OH)_2$ ($T_{n.b.p} = 558.2$ K); (5) cyclohexylbenzene $C_6H_{11}C_6H_5$ ($T_{n.b.p} = 510.7$ K); (6) isobutyraldehyde $(CH_3)_2CHCHO$ ($T_{n.b.p} = 335.2$ K); (7) caproamide $CH_3(CH_2)_4CONH_2$; (8) ethyl caprylate $CH_3(CH_2)_6COOC_2H_5$ ($T_{n.b.p} = 481$ K); (9) acetophenone $C_6H_5COCH_3$ ($T_{n.b.p} = 475$ K); (10) hexahydromesitylene, $C_6H_9(CH_3)_3$ (*trans*) ($T_{n.b.p} = 412$ K); (11) *p*-cymene $CH_3C_6H_4CH(CH_3)_2$ ($T_{n.b.p} = 450$ K); (12) monobutyl ether of diethylene glycol $O{\Large<}{\substack{CH_2CH_2OC_4H_9 \\ CH_2CH_2OH}}$ ($T_{n.b.p} = 504.5$ K); (13) 2-nitrothiophene $\boxed{}$ NO_2 ($T_{n.b.p} = 498$ K); and (14) acetic anhydride $(CH_3CO)_2O$ ($T_{n.b.p} = 413$ K).

246. Calculate the composition of the equilibrium mixture for the reaction

$$C_2H_4 + C_4H_{10} \rightleftarrows C_6H_{14}$$

	C_2H_4	C_4H_{10}	C_6H_{14}
$(\Delta G^\circ_{600})_{form}$, kcal/mol	20.92	24.48	43.78
p_{cr}, atm	50.8	36.0	30.7
T_{cr}, K	283	408	500
Z_{cr}	0.27	0.27	0.27

The reaction is conducted at 600 K and 100 atm. The initial mixture contains one mole each of butane and ethylene.

247. Calculate the yield of *n*-heptane that is possible upon the dearomatization of toluene at 800 K and 50 atm.

	$C_6H_5CH_3$	$4H_2$	C_7H_{16}
$\log(K_{800})_{form}$	-17.00	$-$	-21.802
p_{cr}, atm . . .	41.6	12.8	27.0
T_{cr}, K	593	33	540
Z_{cr}	0.27	0.29	0.27

The molar ratio of toluene and hydrogen in the initial mixture is 1 : 4.

248. For the reaction of hydrogenation of toluene, the temperature dependence of the equilibrium constant is expressed by the equation [9]

$$\log K_f = \frac{10\,970}{T} - 20.387 \pm 0.053$$

Calculate the composition of the equilibrium mixture at 650 K and 150 atm.

	$C_6H_5CH_3 +$	$3H_2$	$\rightleftarrows C_6H_{11}CH_3$
T_{cr}, K .	593	33	572
p_{cr}, atm	41.6	12.8	34.3
Z_{cr} . . .	0.27	0.29	0.25

One mole of toluene and three moles of hydrogen are taken for the reaction.

249. What is the theoretical yield of ethane at 1000 K and 70 atm if at the same temperature and 1 atm it is 17.6 mole per cent?

	$C_2H_4 +$	H_2	$\rightleftarrows C_2H_6$
p_{cr}, atm	50.7	12.6	48.8
T_{cr}, K .	282	33	305
Z_{cr} . . .	0.27	0.23	0.25

250. Determine the composition of the equilibrium mixture that can be obtained if the hydration of ethylene is conducted at 500 K and 100 atm.

	$C_2H_4 +$	H_2O	$\rightleftarrows C_2H_5OH$
$(\Delta G^\circ_{500})_{form}$, kcal/mol	19.245	−52.36	−28.47
p_{cr}, atm	50.9	217.7	63.1
T_{cr}, K	283	647	516
Z_{cr}	0.27	0.23	0.25

An equimolecular ratio of the reactants is taken for the reaction.

251. How much propylene can be formed as a result of the hydrogenation of propadiene at 900 K and 140 atm if the initial mixture consists of an equal number of moles of propadiene and hydrogen?

	$C_3H_4 +$	H_2	$\rightleftarrows C_3H_6$
T_{cr}, K	393.7	33	365
p_{cr}, atm . . .	51.8	12.8	45.6
Z_{cr}	0.28	0.29	0.27
$\log (K_{900})_{form}$	−13.412	—	−9.494

252. Determine the composition of the equilibrium mixture obtained upon the hydrogenation of methylacetylene at 1200 K

and 100 atm if the initial mixture is taken in the stoichiometric proportion; at this temperature $\log K_f = -0.827$.

$$C_3H_4 + 2H_2 \rightleftarrows C_3H_8$$

p_{cr}, atm	52.8	12.8	42
T_{cr}, K .	401	32.2	370
Z_{cr} . . .	0.27	0.29	0.28

253. By how much will the yield of ethyl alcohol obtained in the hydration of ethylene at 623 K increase if the pressure in the system is raised from 50 to 150 atm? The equilibrium constant $K_f = 1.07 \times 10^{-3}$. The critical parameters of the reagents are given in Problem 250.

254. The yield of cyclohexane as a result of the hydrogenation of benzene at 548 K and 1 atm is 9.7 mole per cent. Find its theoretical yield at 100 atm and the same temperature.

$$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}$$

p_{cr}, atm	47.7	12.8	40.4
T_{cr}, K .	561	33	554
Z_{cr} . . .	0.27	0.29	0.27

The stoichiometric amounts of benzene and hydrogen are taken for the reaction.

255. Determine the composition of the equilibrium mixture obtained in the hydrocracking of methylcyclohexane at 800 K and 75 atm.

$$C_6H_{11}CH_3 + 2H_2 \rightleftarrows n\text{-}C_4H_{10} + C_3H_8$$

p_{cr}, atm . . .	34.3	12.8	37.5	42
T_{cr}, K	572	33	425	370
Z_{cr}	0.25	0.29	0.27	0.28
$\log (K_{800})_{form}$.	−23.54	—	−12.08	−8.32

The initial mixture contains one mole of toluene and two moles of hydrogen.

256. What yield of cyclohexane can be expected if the hydrocracking of methylcyclohexane is conducted at 800 K and 100 atm?

$$C_6H_{11}CH_3 + H_2 \rightleftarrows C_6H_{12} + CH_4$$

p_{cr}, atm	34.3	12.8	40.0	45.8
T_{cr}, K .	572	33	533	190.7
Z_{cr} . . .	0.25	0.29	0.27	0.29

The initial mixture consists of the same number of moles of toluene and hydrogen. At this temperature $\log K_f = 2.94$.

257. Calculate the composition of the equilibrium mixture formed in the cracking of *n*-nonane at 700 K and 50 atm if the following

reactions proceed:

(I) $n\text{-}C_9H_{20} \rightleftarrows n\text{-}C_5H_{10} + C_3H_6 + CH_4$

(II) $n\text{-}C_9H_{20} \rightleftarrows n\text{-}C_4H_8 + C_3H_8 + C_2H_4$

(III) $n\text{-}C_9H_{20} \rightleftarrows n\text{-}C_4H_8 + C_3H_6 + C_2H_6$
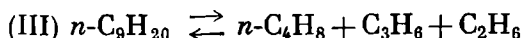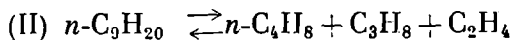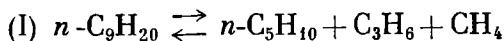
The equilibrium constants at the given temperature are log $K_f^I =$ $= 3.77$, log $K_f^{II} = 1.76$, and log $K_f^{III} = 3.05$. One mole of the n-nonane is taken for the reaction. Take into account that the system is real.

258. Ethylene is alkylated with isobutane at 700 K and 100 atm and the reactants transform into neohexane and 2,2-dimethylbutane. Calculate the composition of the equilibrium mixture if four moles of isobutane react with one mole of ethylene. Take into account that the system is real.

259. In the pyrolysis of propane at 1000 K and 70 atm, the following parallel reactions proceed:

$$C_3H_8 \rightleftarrows C_2H_4 + CH_4$$

$$2C_2H_4 \rightleftarrows C_4H_8$$
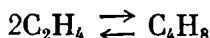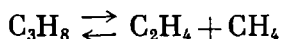
Calculate the composition of the equilibrium mixture, taking into consideration the isomerization of the butenes. One mole of propane is taken for the reaction. The system is real.

260. Calculate the heat of the reaction of synthesis of methyl alcohol

$$CO + 2H_2 \rightarrow CH_3OH$$
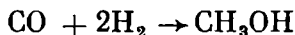
at 600 K and 300 atm. Can the heat of the reaction be taken equal to its standard heat in the given conditions in practical calculations of this reaction?

261. Calculate the enthalpy at the indicated parameters relative to the ideal gaseous state at 0 K for the substances listed below (the values of T, K and p, atm, respectively, are indicated in parentheses): (1) sulphur dioxide SO_2 (298 and 100); (2) ammonia NH_3 (298 and 150); (3) ethylene C_2H_4 (500 and 75); (4) n-octane C_8H_{18} (298 and 100); (5) cumene $C_6H_5C_3H_7$ (600 and 75); (6) ethyl alcohol C_2H_5OH (500 and 50); and (7) chloroform $CHCl_3$ (600 and 75).

262. Calculate the heat of the reactions of hydrocracking of methylcyclohexane at 600 K and 75 atm which proceed in the following directions:

(I) $C_6H_{11}CH_3 + H_2 \rightarrow \text{cyclohexane} + CH_4$

(II) $C_6H_{11}CH_3 + 2H_2 \rightarrow C_4H_{10} + C_3H_8$
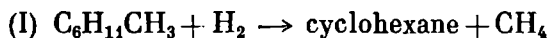
263. Can we use the standard heat of the reaction in calculating the heat balance for the reactor used in the dearomatization of toluene

$$C_6H_5CH_3 + 4H_2 \rightleftarrows C_7H_{16} \text{ (}n\text{-heptane)}$$
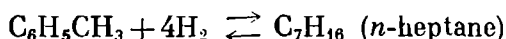
if the reaction is conducted at from 600 to 700 K and 50 atm?

264. What is the heat of the reaction of cracking of n-nonane at 800 K and 75 atm? Cracking proceeds in the following directions:

(1) $C_9H_{20} \rightarrow C_4H_8$ (1-butene) $+ n\text{-}C_5H_{12}$

(2) $C_9H_{20} \rightarrow 2C_3H_6 + C_3H_8$

(3) $C_9H_{20} \rightarrow iso\text{-}C_4H_8 + C_3H_6 + C_2H_6$
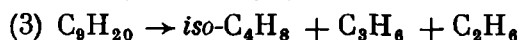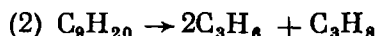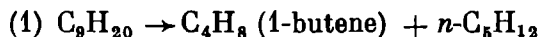
265. What error is made in the value of the heat of the following reactions if no account is taken of the change in enthalpy with pressure of the reagents:

(1) $2CH_4 + O_2 \rightarrow C_2H_5OH + H_2O$ at   700 K   and   100 atm

(2) $2CH_4 + \frac{1}{2}O_2 \rightarrow C_2H_6 + H_2O$ at 700 K and 100 atm

(3) $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$ (cyclohexane) at 500 K and 70 atm

(4) $n\text{-}C_8H_{18} \rightarrow 4H_2 + p\text{-}C_6H_4(CH_3)_2$ at   600 K   and   50 atm
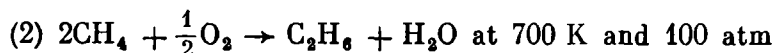
Combined Problems

266. Calculate the equilibrium constant of the reaction of hydrogenation of cumene at 500 K and 1 atm; find $(\Delta G^\circ_{500})_{form}$ for cumene (isopropylbenzene) using the method of Chermin and van Krevelen. Compare the calculated value with the one found experimentally by A. Vvedensky and his co-workers [9] for this reaction at 498 K, i.e. log $K_p = 1.426$. What discrepancy will be obtained in the composition of the equilibrium mixture when using the calculated and the experimentally determined equilibrium constants if a stoichiometric proportion of the reactants is taken for the reaction?

267. At what temperature is the reaction of dehydrogenation of diphenylmethane to fluorene
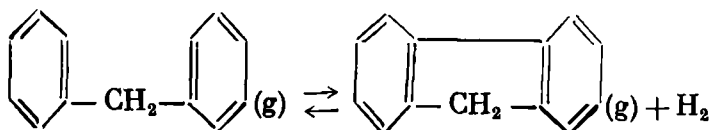
possible in standard conditions?

268. What amounts of alkene-aromatic hydrocarbons (in mole per cent) are formed from isopropylbenzene according to the reac-

tions

$$C_6H_5CH(CH_3)_2(g) \rightleftarrows C_6H_5CH = CH_2(g) + CH_4$$

$$C_6H_5CH(CH_3)_2(g) \rightleftarrows C_6H_5C = CH_2(g) + H_2$$
$$\underset{CH_3}{\mid}$$
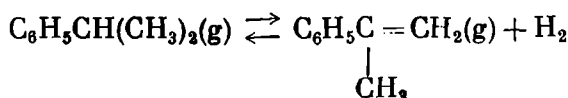
at 1000 K and 1 atm if one mole of cumene is taken for the reaction?

269. Determine the composition of the equilibrium mixture obtained in the nitration of α-nitronaphthalene at 298 K and 1 atm. The initial mixture is equimolecular. Assume that the reaction proceeds in the gaseous phase.
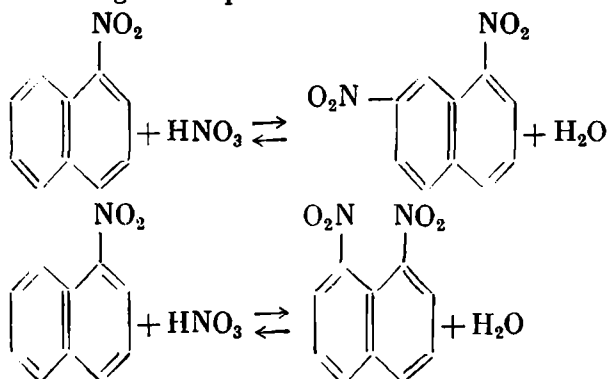
Calculate the thermodynamic parameters of the nitronaphthalenes using Andersen's method.

270. How much 3,5-diethylphenol can be formed if phenol is alkylated with ethyl alcohol at 600 K and 1 atm, and if the stoichiometric amount of the reactants is taken

$$C_6H_5OH(g) + 2C_2H_5OH(g) \rightleftarrows HOC_6H_3(C_2H_5)_2(g) + 2H_2O(g)$$
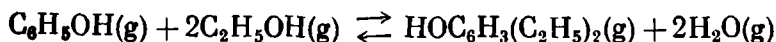
271. At what temperature is the oxidation of cumene to phenol and acetone possible (the reaction is conducted in the gaseous phase in standard conditions)

$$C_6H_5C_3H_7 + O_2 \rightleftarrows C_6H_5OH + (CH_3)_2CO$$

272. The reaction

$$Cl_2 + H_2O(g) \rightleftarrows 2HCl(g) + \frac{1}{2}O_2$$
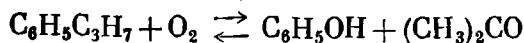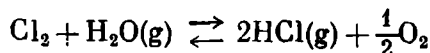
proceeds at an elevated temperature. (1) Derive the relationship $\Delta G^\circ = \varphi(T)$ (plot a graph); (2) calculate the composition of the equilibrium mixture at 500 K and 1 atm if the initial mixture contains one mole each of Cl_2 and H_2O; and (3) calculate the composition of the equilibrium mixture at 500 K, 100 atm, and the composition of the initial mixture indicated above.

273. The following reactions are possible upon the irradiation of an aqueous solution saturated with acetylene:

$$H_2O \rightleftarrows H + OH$$

$$2H_2O \rightleftarrows H_2O_2 + H_2$$

$$C_2H_2 + H_2O \rightleftarrows CH_3CHO \text{ (acetaldehyde)}$$

$$C_2H_2 + H_2O_2 \rightleftarrows HOCH_2CHO \text{ (glycolaldehyde)}$$

$$2C_2H_2 + H_2O \rightleftarrows CH_3CH = CHCHO \text{ (crotonaldehyde)}$$

$$C_2H_2 + H_2O \rightleftarrows H_2C \underset{\diagdown \ O \ \diagup}{\quad\quad} CH_2 \text{ (ethylene oxide)}$$

$$C_2H_2 + 2OH \rightleftarrows H_2 + OHCCHO \text{ (oxalic aldehyde)}$$
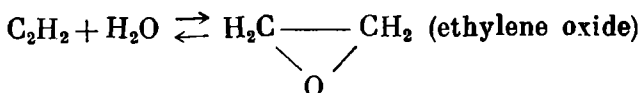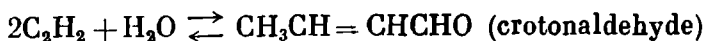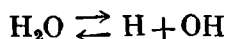
Assuming that the reactions proceed in the gaseous phase at 1 atm, determine which of the above reactions proceeds owing to irradiation at 400 K.

274. For the reaction

$$3H_2 + SO_2 \rightleftarrows H_2S + 2H_2O$$
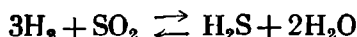
(1) find and plot the graphical relationships $\Delta H° = f(T)$ and $\Delta G° = f'(T)$; (2) calculate the composition of the equilibrium mixture at 1200 K if three moles of hydrogen and one mole of sulphur dioxide are taken for the reaction, and if the system is assumed to be ideal; and (3) calculate the composition of the equilibrium mixture at 100 atm [use the remaining conditions given in (2)].

275. What theoretical yield of alcohols is possible in the hydration of 2-pentene at 300 K and 45 atm:

$$C_5H_{10}(g) + H_2O \rightleftarrows CH_3CH_2CH_2CH_2CH_2OH(g)$$

$$C_5H_{10}(g) + H_2O \rightleftarrows CH_3CH_2CH_2CHOHCH_3(g)$$

Assume that the system is ideal. The process occurs in the gaseous phase. An equal number of moles of the reactants is taken. Calculate the lacking thermodynamic quantities according to Andersen's method.

276. Which of the following reactions will form the maximum amount of acrylonitrile if they are not attended by side reactions and are conducted at 500 K and 1 atm in the gaseous phase:

$$C_2H_2 + HCN \rightleftarrows CH_2 = CHCN$$

$$CH_2 = CHCH_2NH_2 + O_2 \rightleftarrows CH_2 = CHCN + 2H_2O$$

$$C_3H_6 + NH_3 + 1\frac{1}{2}O_2 \rightleftarrows CH_2 = CHCN + 3H_2O$$

$$H_2C\underset{O}{\overset{}{\diagdown\diagup}}CH_2 + HCN \rightleftarrows CH_2 = CHCN + H_2O$$

$$CH_3CN + HCHO \rightleftarrows CH_2 = CHCN + H_2O$$

$$CH_3CH_2COOH + NH_3' + \frac{1}{2}O_2 \rightleftarrows CH_2 = CHCN + 3H_2O$$
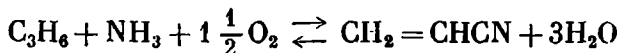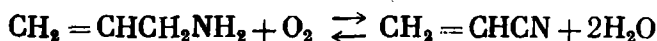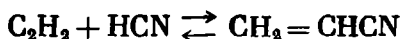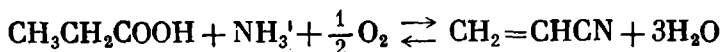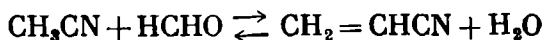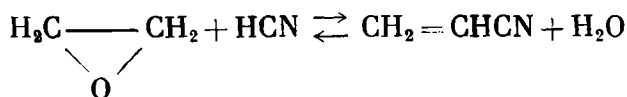
277. The formation of the following products is possible in the oxidation of isopropylbenzene:

$$C_6H_5CH(CH_3)_2 + O_2 \rightleftarrows CH_3COCH_3 + C_6H_5OH$$

$$C_6H_5CH(CH_3)_2 + O_2 \rightleftarrows CH_3OH + C_6H_5COCH_3 \quad (acetophenone)$$

$$C_6H_5CH(CH_3)_2 + O_2 \rightleftarrows \frac{1}{2}O_2 + C_6H_5COH(CH_3)_2 \quad (dimethylphen-$$
$$ylcarbinol)$$
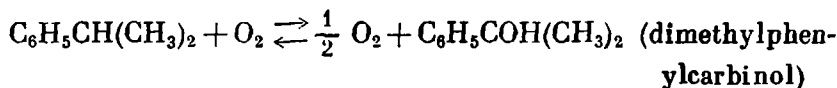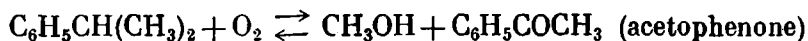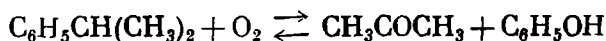
Which direction will prevail at 298 K if the reaction is conducted in the gaseous phase?

278. Calculate the theoretical yield of lactic acid according to the reaction

$$CH_3CHO + H_2O + CO \rightleftarrows CH_3CHOHCOOH$$
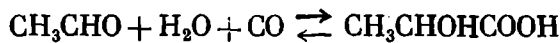
conducted in the gaseous phase at 500 K and 800 atm. Calculate the lacking values of $(\Delta G^\circ_{500})_{form}$ according to the method of Chermin and van Krevelen, and the critical parameters of lactic acid according to Lydersen's method. Lactic acid boils at 395 K.

279. In the presence of a catalyst, diacetone alcohol transforms into acetone and mesityl oxide:

$$CH_3COCH_2COH(CH_3)_2 \rightleftarrows 2CH_3COCH_3$$

$$CH_3COCH_2COH(CH_3)_2 \rightleftarrows H_2O + CH_3COCHC(CH_3)_2$$
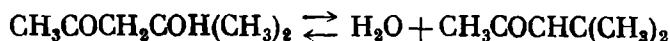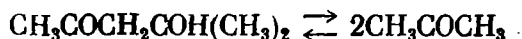
How does a change in temperature from 400 to 600 K affect the composition of the equilibrium mixture? One mole of diacetone alcohol is taken for the reaction which is conducted in the gaseous phase. Calculate the values of $(\Delta G^\circ_T)_{form}$ for the reagents using the method of Chermin and van Krevelen.

280. Propyl alcohol is produced by the hydrogenation of propionic aldehyde at 600 K and 1 atm:

$$CH_3CH_2CHO(g) + H_2 \rightleftarrows CH_3CH_2CH_2OH(g)$$
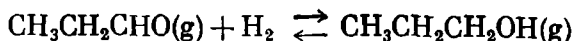
The propionic aldehyde is the product of hydroxysynthesis conducted at 600 K and 100 atm:

$$C_2H_4 + CO + H_2 \rightleftarrows CH_3CH_2CHO(g)$$
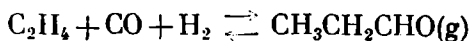
Calculate the theoretical yield of alcohol for an initial mixture consisting of an equal number of moles of ethylene, hydrogen, and carbon monoxide. Calculate the lacking values of $(\Delta G^{\circ}_{600})_{form}$ according to the method of Chermin and van Krevelen. The aldehyde boils at 322 K.

281. Chloroform CH_3Cl can be obtained in three ways. Show which of them will give the greatest theoretical yield at 300 K if the reactions are conducted in the gaseous phase:

(1) $CH_4 + Cl_2 \rightleftarrows CH_3Cl + HCl$

$CH_3Cl + Cl_2 \rightleftarrows CH_2Cl_2 + HCl$

$CH_2Cl_2 + Cl_2 \rightleftarrows CHCl_3 + HCl$

(2) $CH_3CHO + 3Cl_2 \rightleftarrows CCl_3CHO + 3HCl$

$CCl_3CHO + H_2O \rightleftarrows CHCl_3 + HCOOH$

(3) $(CH_3)_2CO + 3Cl_2 \rightleftarrows Cl_3CCOCH_3 + 3HCl$

$Cl_3CCOCH_3 + H_2O \rightleftarrows CHCl_3 + CH_3COOH$
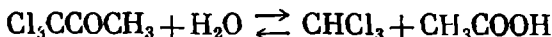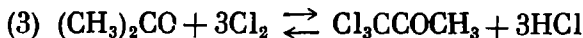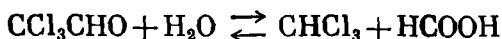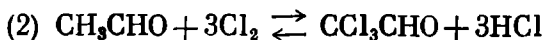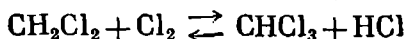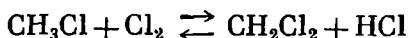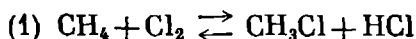
282. Determine the theoretical yield of adipic acid produced from tetrahydrofuran in the presence of a catalyst:

$$
\begin{matrix}
H_2C - CH_2 \\
| \quad\quad | \\
H_2C \quad CH_2 \\
\diagdown \diagup \\
O
\end{matrix}
\; + 2CO + H_2O \rightleftarrows HOOC(CH_2)_4COOH
$$
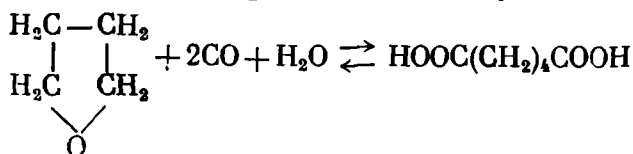
The reaction is conducted at 800 K and 100 atm in the gaseous phase; stoichiometric amounts of the reactants are taken.

283. It is possible to produce isophorone used as a solvent by the condensation of acetone. By how much will the theoretical yields differ (in mole per cent) if no account is taken of the fact that the state of the system is real? The reaction is conducted at 500 K and 35 atm with three moles of acetone:

$$3(CH_3)_2CO \rightleftarrows H_3C - \text{(isophorone ring)} \begin{matrix} CH_3 \\ \diagup \\ \diagdown \\ CH_3 \end{matrix} + 2H_2O$$
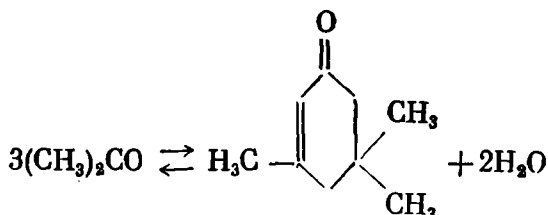
284. Ethylene cyanohydrin is obtained by the reaction

$$
\begin{matrix}
H_2C \rule{1cm}{0.4pt} CH_2(g) \\
\diagdown \quad \diagup \\
O
\end{matrix}
+ HCN(g) \rightleftarrows CH_2OHCH_2CN(g)
$$
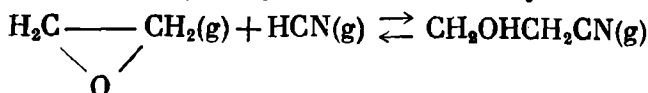
How does a change in temperature from 300 to 800 K affect the theoretical yield of ethylene cyanohydrin if the state of the system is standard?

285. The oxidation of propylene can proceed in three directions:

$$C_3H_6 + \frac{1}{2} O_2 \rightleftarrows (CH_3)_2CO$$

$$C_3H_6 + \frac{1}{2} O_2 \rightleftarrows CH_3CH_2CHO$$

$$C_3H_6 + \frac{1}{2} O_2 \rightleftarrows H_2C \underset{\underset{O}{\diagdown \diagup}}{\overline{\qquad}} CH - CH_3$$
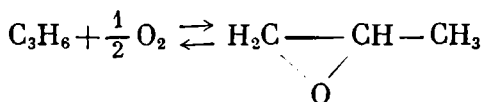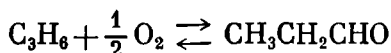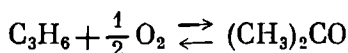
Plot a graph of the temperature dependence of the change in the yield of the products for the interval from 300 to 800 K provided that the stoichiometric amounts of the reactants are taken for the reactions, and the total pressure in the system is $p = 1$ atm. All the reactions proceed in the gaseous phase.

286. Is it possible to produce 4,4-dimethyl-1,3-dioxane according to the reaction

$$2HCHO + iso\text{-}C_4H_8 \rightleftarrows O \underset{\overset{\diagdown}{\underset{\diagup}{\underset{C - C}{\underset{H_2 \quad H_2}{}}}}}{\overset{\diagup}{\overset{\overset{H_2}{C - O}}{\diagdown}}} C(CH_3)_2$$
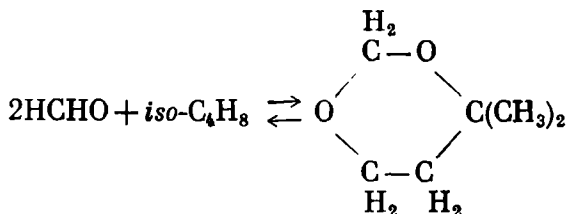
if it is conducted in the gaseous phase at 500 K and 30 atm?

287. What is the theoretical yield of triethylamine produced by the consecutive introduction of ethylene into the previously obtained product:

$$C_2H_4 + NH_3 \rightleftarrows C_2H_5NH_2(g)$$

$$C_2H_4 + C_2H_5NH_2(g) \rightleftarrows (C_2H_5)_2NH(g)$$

$$C_2H_4 + (C_2H_5)_2NH(g) \rightleftarrows (C_2H_5)_3N(g)$$
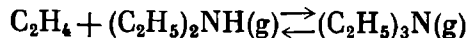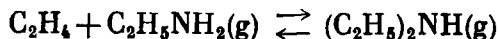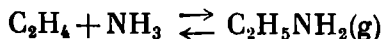
Each reaction is conducted independently at 500 K and 800 atm using stoichiometric amounts of the substances. Perform the calculations per mole of the initial ammonia.

288. Tetrahydrofuran is obtained from furfurol by consecutively conducting decarbonylation and hydrogenation. If both reactions are conducted at 600 K, then how much tetrahydrofuran can be formed from a mole of furfurol? The reactions are conducted in the

gaseous phase at 1 atm:
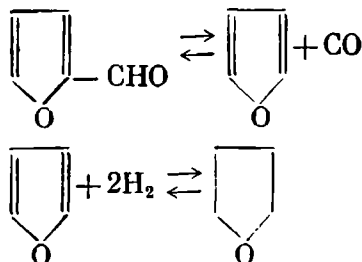
289. Isomerization of propylene oxide results in the formation of acetone, propionic aldehyde, and allyl alcohol:

H_2C——$CHCH_3(g) \rightleftarrows CH_3CH_2CHO(g)$

H_2C——$CHCH_3(g) \rightleftarrows CH_3COCH_3(g)$

H_2C——$CHCH_3(g) \rightleftarrows CH_2 = CHCH_2OH(g)$
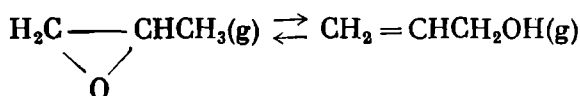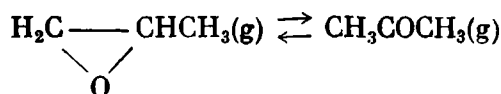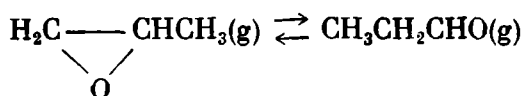
Plot a graph of the temperature dependence of the composition of the equilibrium mixture for the interval from 300 to 1000 K and for 1 atm.

290. The alkylation of aniline with ethers in the vapour phase makes it possible to produce mono- and dialkyl anilines. Show how the theoretical yield of monomethyl- and dimethyl aniline varies with a change in the temperature from 600 to 800 K for the reactions

$$C_6H_5NH_2(g) + (CH_3)_2O(g) \rightleftarrows C_6H_5NHCH_3(g) + CH_3OH(g)$$

$$C_6H_5NHCH_3(g) + (CH_3)_2O(g) \rightleftarrows C_6H_5N(CH_3)_2(g) + CH_3OH(g)$$
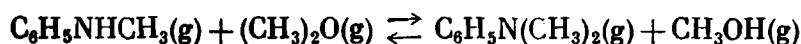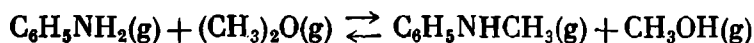
if the process is conducted with one mole of aniline and two moles of the ether at 1 atm.

Appendices

The following quantities are tabulated in this Appendix:

$(\Delta H^{\circ}_{298})_{comb}$ = standard heat of combustion of a compound at 298.15 K, kcal/mol

$(\Delta H^{\circ}_{298})_{form}$ = standard heat of formation of a compound from simple substances (the change in the enthalpy as a result of the reaction of formation of one mole of the given compound from simple substances in standard conditions at 298.15 K), kcal/mol

$(\Delta G^{\circ}_{298})_{form}$ = standard Gibbs energy (the change in the Gibbs energy as a result of the reaction of formation of one mole of the given compound from simple substances in standard conditions at 298.15 K), kcal/mol

S°_{298} = absolute value of the entropy of a compound in standard conditions at 298.15 K, cal/mol·K

$(C^{\circ}_{p})_{298}$ = true molar standard heat capacity of a compound at p = const and 298.15 K, cal/mol·K; for a temperature differing from 298.15 K, the value of C°_{p} is computed with the aid of the coefficients given in the table by using the equation

$$C^{\circ}_{p} = a + bT + cT^{2}$$

T_{cr} = critical temperature, K

p_{cr} = critical pressure, atm

Z_{cr} = compression factor at the critical parameters.

The above data are given for selected simple substances, inorganic compounds, and organic compounds, the latter including hydrocarbons, alcohols, ethers, esters, aldehydes, ketones, acids, halogen derivatives, nitrogen derivatives, and sulphur derivatives.

Simple Substances

Molecular formula	Name	State	$-(\Delta H^\circ_{298})_{comb}$	$(\Delta H^\circ_{298})_{form}$	$(\Delta G^\circ_{298})_{form}$	S°_{298}	$(C^\circ_p)_{298}$	Heat capacity — Coefficients of equation $C^\circ_p = f(T)$			Temperature interval, K	T_{cr}	p_{cr}	z_{cr}
								a	$b \times 10^3$	$c \times 10^6$				
Br_2	Bromine	g	—	−7.340	0.751	58.636	8.60	8.89	0.165	—	300-1500	584.2	102	0.306
		lq	—	0	0	36.4	8.50	8.50	—	—	298	—	—	—
C	Diamond	c	—	0.453	0.685	0.583	1.45	2.18	3.16	—	298-1200	—	—	—
C	Graphite	c	—	0	0	1.361	2.07	4.10	1.02	—	298-2300	—	—	—
Cl_2	Chlorine	g	—	0	0	53.286	8.11	8.77	0.25	—	273-1500	417.2	76.1	0.276
F_2	Fluorine	g	68.310	0	0	48.6	7.52	8.29	0.44	—	273-2000	144.2	55	0.292
H_2	Hydrogen	g	—	0	0	31.211	6.89	6.95	−0.20	0.48	300-1500	33.3	12.8	0.292
I_2	Iodine	c	—	0	0	27.9	13.14	9.59	11.90	—	298-386.8	—	—	—
		g	—	14.876	0.463	62.28	8.81	8.81	—	—	298	826.2	—	0.248
N_2	Nitrogen	g	—	0	0	45.787	6.96	6.66	1.02	—	273-2500	126.2	33.5	0.291
O_2	Oxygen	g	—	0	0	49.003	7.02	7.52	0.81	—	273-2000	154.8	50.1	0.292
O_3	Ozone	g	—	34.000	39.060	56.8	9.12	9.12	—	—	298	261.1	54.6	0.272
P_2	Phosphorus	g	—	33.820	24.600	52.13	7.63	8.57	0.275	—	273-2000	—	—	—
P_4	Phosphorus	g	—	13.120	5.820	66.90	16.0	—	—	—	298	—	—	—
P	Phosphorus, white	c	—	0	0	10.6	5.55	5.55	—	—	273-317	—	—	—
S	Sulphur, monoclinic	c	—	0.071	0.023	7.78	5.65	3.58	6.95	—	368.6-392	—	—	—
S	Sulphur, rhombic	c	—	0	0	7.62	5.40	3.58	6.24	—	273-368.6	1313.2	116	—
S_2	Sulphur	g	—	29.860	18.190	54.41	7.78	8.63	0.26	—	273-2000	—	—	—
S_8	Sulphur	g	—	24.350	10.560	102.76	37.15	—	—	—	—	—	—	—

Inorganic Compounds

	Name	State									Temp. range			
CO	Carbon monoxide	g	67.620	-26.416	-32.808	47.301	6.965	6.6	1.2	—	298-2500	132.9	34.5	0.294
CO₂	Carbon dioxide	g	—	-94.052	-94.260	51.06	8.874	10.55	2.16	—	298-2500	304.2	72.9	0.274
COCl₂	Phosgene	g	—	-53.300	-50.310	69.13	14.51	16.051	2.894	—	258-1000	455.2	56	0.285
COS	Carbon oxysulphide	g	132.200	-32.800	-40.450	55.34	9.92	11.50	2.02	—	298-1800	378.2	61	—
CS₂	Carbon disulphide	g	—	27.550	15.550	56.84	10.90	12.45	1.6	—	298-1800	552.2	78	—
CS₂	Carbon disulphide	lq	257.000	21.000	15.200	36.10	18.10	18.10	—	—	293	—	—	—
HBr	Hydrogen bromide	g	—	-8.660	-12.720	47.44	6.96	6.25	1.40	—	298-1600	363.2	84.0	—
HCl	Hydrogen chloride	g	—	-22.063	-22.769	44.617	6.96	6.34	1.10	—	298-2000	324.6	81.5	0.266
HF	Hydrogen fluoride	g	—	-84.200	-64.700	41.47	6.96	6.62	0.70	—	273-2000	461.2	64.4	0.223
HI	Hydrogen iodide	g	—	6.200	0.310	49.31	6.96	6.29	1.42	—	298-1000	424.2	82.0	—
HCN	Hydrogen cyanide	g	—	31.200	28.700	48.23	8.58	8.92	3.10	—	298-2000	456.7	48.9	—
		lq	—	25.200	29.86	59.427	12.40	—	—	—	—	—	—	—
HNO₃	Nitric acid	g	—	-31.990	-17.590	63.62	14.0	14.0	—	—	298-500	—	—	—
		lq	—	-41.404	-19.100	37.19	26.26	26.26	—	—	300	—	—	—
H₂O	Water	g	—	-57.798	-54.635	45.106	8.023	7.20	2.70	—	273-2000	—	—	—
		lq	—	-68.317	-56.690	16.716	17.996	17.996	—	—	298	647.4	218.3	0.23
		c	—	-69.754	—	9.4	—	-0.047	33.5	—	273	—	—	—
H₂O₂	Hydrogen peroxide	g	—	-32.530	-25.200	55.56	10.31	—	—	—	—	—	—	—
		lq	—	-44.840	-28.230	24.44	19.67	19.67	—	—	273-291	—	—	—
H₂S	Hydrogen sulphide	g	138.380	-4.815	-7.892	49.15	8.12	7.00	3.75	—	273-1300	373.6	88.9	—

Appendix 1 (continued)

Molecular formula	Name	State	$-(\Delta H^\circ_{298})$comb	(ΔH°_{298})form	(ΔG°_{298})form	S°_{298}	$(C^\circ_p)_{298}$	Coefficients of equation $C^\circ_p = f(T)$			Temperature interval, K	T_{cr}	p_{cr}	z_{cr}
								a	$b \times 10^3$	$c \times 10^6$				
H₂SO₄	Sulphuric acid	lq	—	−193.910	−164.100	37.49	32.88	32.88	—	—	298	—	—	—
NH₃	Ammonia	g	—	−11.040	−3.976	46.01	8.52	7.12	6.09	—	273–1400	405.6	111.5	0.242
NO	Nitric oxide	g	—	21.477	21.600	50.239	7.137	7.07	0.92	—	273–1500	180.3	64.6	0.251
NO₂	Nitrogen dioxide	g	—	8.090	12.390	57.47	9.06	10.26	2.04	—	—	431.0	100.0	—
N₂O	Nitrous oxide	g	—	19.490	24.760	52.58	9.25	10.92	2.06	—	273–1500	309.7	71.7	0.271
N₂O₄	Nitrogen tetroxide	g	—	2.309	23.490	72.73	18.9	20.05	9.50	—	—	431.2	99	—
NOCl	Nitrosyl chloride	g	—	12.570	15.860	63.0	9.25	—	—	—	—	438.2	92.4	—
PH₃	Phosphine	g	—	2.210	4.360	50.2	8.63	—	—	—	—	—	—	—
PCl₃	Phosphorus trichloride	g	—	−68.600	−64.000	74.49	17.17	20.068	0.289	—	298–1000	324.5	64.5	—
PCl₅	Phosphorus pentachloride	g	—	−89.600	−73.000	87.11	26.96	4.739	107.33	−119.20	298–500	—	—	—
SO₂	Sulphur dioxide	g	—	−70.960	−71.790	59.4	9.51	11.40	1.714	—	298–1800	430.7	77.8	0.268
SO₃	Sulphur trioxide	g	—	−94.450	−88.520	61.24	12.1	13.70	6.42	—	273–900	491.4	83.8	0.262
SO₂Cl₂	Sulphuryl chloride	g	—	−82.040	−74.060	74.6	18.51	12.84	19.00	—	298–500	—	—	—
		lq	—	−93.000	−71.560	—	31.5	—	—	—		—	—	—
SiF₄	Silicon tetrafluoride	g	—	−370.800	−360.590	66.05	16.88	22.7	2.05	—	273–1600	259.1	36.7	—

	Formula	Compound	State												
	SiCl₄	Silicon tetra-chloride	g	—	-151.800	-142.300	70.06	21.63	21.63	—	—	298	506.2	37.1	—
	SiH₄	Silane	g	—	-14.800	-9.400	48.7	10.24	11.05	8.78	—	298-1800	269.7	47.8	—

Organic Compounds

(a) *Hydrocarbons*

	Formula	Compound	State												
	CH₄	Methane	g	212.800	-17.889	-12.140	44.5	8.536	4.171	14·45	0.267	298-1500	191.1	45.8	0.29
	C₂H₂	Ethyne (acetylene)	g	310.620	54.194	50.000	47.997	10.499	5.607	20.499	-13.944	298-1500	309.2	61.6	0.274
	C₂H₄	Ethene (ethylene)	g	337.230	12.496	16.282	52.45	10.41	1.003	36.948	-19.381	298-1500	293	50.5	0.270
	C₂H₆	Ethane	g	372.820	-20.236	-7.860	54.85	12.585	1.074	43.561	-17.891	298-1500	305.5	48.2	0.285
	C₃H₄	Propyne (methylacetylene)	g	463.110	44.320	46.500	59.30	14.50	4.41	37.61	14.38	—	401.0	52.8	0.270
	C₃H₄	Propadiene (allene)	g	464.710	45.920	48.370	58.30	14.10	3.62	36.17	-12.16	273-1200	393.2	43.6	0.281
	C₃H₆	Propene (propylene)	g	491.990	4.879	14.990	63.80	15.27	0.790	56.372	-28.107	298-1500	365.0	45.6	0.274
	C₃H₆	Cyclopropane	g	—	12.740	24.940	56.81	13.2	—	—	—	—	397.8	54.2	—
	C₃H₈	Propane	g	530.600	-24.820	-5.614	64.51	17.57	-1.147	73.449	-38.279	298-1500	370.0	42.0	0.277
	C₃H₈	Propane	lq	—	-28.643	—	—	—	—	—	—	—	—	—	—
	C₄H₆	1,3-Butadiene (divinyl)	g	607.490	26.330	36.010	66.62	19.01	-0.707	81.282	-53.463	298-1500	425.2	42.7	0.271
	C₄H₆	1-Butyne (ethylacetylene)	g	620.640	39.480	48.300	69.51	19.46	3.217	64.540	35.659	—	463.7	—	—
	C₄H₆	2-Butyne	g	616.130	34.970	44.320	67.71	18.71	3.605	57.786	26.705	—	488.7	—	—
	C₄H₆	1,2-Butadiene	g	619.930	38.770	47.430	70.03	19.51	—	—	—	—	—	—	—
	C₄H₈	1-Butene	g	649.450	-0.030	17.090	73.48	20.47	5.132	61.76	-19.322	298-1500	419.6	39.7	0.277
	C₄H₈	cis-2-Butene	g	647.810	-1.360	16.050	71.90	18.86	2.047	64.311	19.834	298-1500	434.6	41	0.268

Appendix 1 (continued)

Molecular formula	Name	State	$-(\Delta H°_{298})_{comb}$	$(\Delta H°_{298})_{form}$	$(\Delta G°_{298})_{form}$	$S°_{298}$	$(C°_p)_{298}$	Heat capacity Coefficients of equation $C°_p=f(T)$			Temperature interval, K	T_{cr}	p_{cr}	z_{cr}
								a	$b×10^3$	$c×10^6$				
C_4H_8	trans-2-Butene	g	646.810	−2.670	15.050	70.86	20.99	2.003	73.504	−35.434	298–1500	428.6	41.5	0.263
C_4H_8	2-Methylpropene (isobutylene)	g	645.430	−4.040	13.880	70.17	21.30	1.693	76.872	−39.692	298–1500	417.9	39.5	0.270
C_4H_{10}	n-Butane	g	887.650	−30.150	−4.100	74.12	23.29	0.112	92.107	−47.534	298–1500	425.2	37.5	0.274
		lq		−35.290										
C_4H_{10}	Isobutane	g	685.650	−32.150	−5.000	70.42	23.14	−1.635	97.907	−52.712	298–1500	407.1	36.0	0.283
		lq		−37.870										
C_5H_8	1-Pentyne	g	778.030	34.500	50.160	79.10	25.50	4.444	83.282	44.98				
C_5H_8	2-Pentyne	g	774.330	30.800	48.410	79.30	23.59	2.643	81.570	40.486				
C_5H_8	2-Methyl-1,3-butadiene (isoprene)	g	761.610	18.090	34.850	75.44	25.0							
		lq		11.800	34.790	54.8	38.6							
C_5H_8	Cyclopentene	g		7.870	26.480	59.23	17.95					506.2	47.2	0.272
		lq		1.160	19.360	48.10	29.24							
C_5H_{10}	1-Pentene	g	806.850	−5.000	18.960	82.65	26.19	1.788	101.454	−55.427		464.8	40	0.266
		lq				62.75	37.12							
C_5H_{10}	cis-2-Pentene	g	805.340	−6.710	17.170	82.76	24.32	−3.351	109.623	−60.345		475.6	40.4	0.266
		lq		−14.860	15.430	61.81	36.26							
C_5H_{10}	trans-2-Pentene	g	804.260	−7.590	16.760	81.36	25.92	1.490	99.696	−52.863		475.6	40.4	0.266
		lq		−14.860	15.220	61.31	37.52							
C_5H_{10}	2-Methyl-1-butene	g	803.170	−8.680	15.510	81.73	26.69	0.495	103.985	−57.404				0.274

Formula	Compound	State												
C_5H_{10}	3-Methyl-1-butene	g	804.930	-6.920	17.870	79.70	28.35	3.270	99.735	-55.151	—	464.8	33.9	—
		lq	—	-15.200	15.110	60.54	37.30	—	—	—	—	—	—	—
C_5H_{10}	2-Methyl-2-butene	g	—	-10.170	14.260	80.92	25.10	0.130	99.118	-50.437	—	470.2	34	0.266
		lq	—	—	—	60.0	36.52	—	—	—	—	—	—	—
C_5H_{10}	Cyclopentane	g	793.390	-18.460	9.230	70.0	19.82	-13.0	130.45	-73.547	258-1500	511.8	44.6	0.276
		lq	—	-25.300	8.700	48.82	30.29	—	—	—	298	—	—	—
C_5H_{12}	n-Pentane	g	845.160	-35.000	-2.000	83.40	28.73	0.345	113.88	-59.849	298-1500	469.8	33.3	0.269
		lq	—	-41.360	-2.250	62.92	41.3	36.29	—	—	298	—	—	—
C_5H_{12}	2-Methylbutane (isopentane)	g	843.240	-36.920	-3.500	82.12	28.39	-2.22	123.739	-70.005	298-1500	461	33.7	0.268
		lq	—	-42.850	-3.590	62.52	39.40	—	—	—	298	—	—	—
C_5H_{12}	2,2-Dimethyl-propane (neopentane)	g	840.490	-39.670	-3.640	73.23	29.07	-3.61	131.114	-77.180	298-1500	433.8	31.6	0.269
		lq	—	-44.980	-3.370	54.5	—	—	—	—	—	—	—	—
C_6H_6	Benzene	g	789.080	19.820	30.989	64.34	19.52	-8.102	112.78	-71.306	298-1500	562.7	48.6	0.274
		lq	—	11.718	29.756	41.30	32.45	14.22	60.95	—	281-353	—	—	—
C_6H_{10}	Cyclohexene	g	—	-9.600	17.120	74.2	25.10	—	—	—	—	559.2	41.8	—
		lq	—	-17.600	15.960	51.67	34.9	—	—	—	—	—	—	—
C_6H_{12}	1-Hexene	g	964.260	-9.960	20.940	91.93	31.63	2.063	123.004	-67.401	298-1500	504.0	31.1	0.261
		lq	—	-17.280	19.950	70.55	43.81	—	—	—	—	—	—	—
C_6H_{12}	Methylcyclo-pentane	g	948.720	-25.500	8.550	81.24	26.24	-11.983	152.447	-87.117	298-1500	532.8	37.4	0.273
		lq	—	-33.070	7.530	59.26	37.6	—	—	—	—	—	—	—
C_6H_{12}	Cyclohexane	g	944.790	-29.430	7.590	71.28	25.40	-16.172	162.393	-91.004	298-1500	554.2	40.6	0.271
		lq	—	-37.340	6.370	48.85	37.4	—	—	—	—	—	—	—
C_6H_{14}	n-Hexane	g	1002.570	-39.960	-0.070	92.83	34.20	0.737	135.226	-71.79	298-1500	507.9	29.9	0.264
		lq	—	-47.520	-1.030	70.72	46.59	—	—	—	298	—	—	—
C_6H_{14}	2-Methylpen-tane	g	1000.870	-41.660	-1.220	90.95	34.46	1.361	125.712	-48.147	298-1000	497.9	29.9	0.270
		lq	—	-48.820	-1.970	69.51	—	—	—	—	298	—	—	—
C_6H_{14}	3-Methylpen-tane	g	1001.510	-41.020	-0.510	90.77	34.20	2.621	123.504	-47.104	298-1000	504.7	30.8	0.273
		lq	—	-48.280	-1.340	69.22	44.8	—	—	—	—	—	—	—

Appendix 1 *(continued)*

Molecular formula	Name	state	$-(\Delta H^\circ_{298.comb})$	$(\Delta H^\circ_{298})_{form}$	$(\Delta G^\circ_{298})_{form}$	S°_{298}	$(c^\circ_p)_{298}$	Heat capacity — Coefficients of equation $C^\circ_p = f(T)$			Temperature interval, K	T_{cr}	p_{cr}	Z_{cr}
								a	$b \times 10^3$	$e \times 10^6$				
C_6H_{14}	2,2-Dimethyl-butane	g	998.170	−44.350	−2.370	85.72	33.91	0.593	133.0	−52.878	298-1000	486.7	30.7	0.273
		lq	—	−51.000	−2.900	65.08	—	—	—	—	—	—	—	—
C_6H_{14}	2,3-Dimethyl-butane	g	1000.004	−42.490	−0.980	87.42	33.59	1.298	126.929	−49.133	—	560.3	30.9	0.27
		lq	—	−49.480	−1.690	66.36	44.1	—	—	—	—	—	—	—
C_7H_8	Toluene	g	943.580	11.050	29.228	76.42	24.80	−8.098	133.137	−81.829	298-1500	592.0	41.6	0.271
		lq	—	2.967	27.282	52.48	32.55	14.25	78.15	—	281-382	—	—	—
C_7H_{14}	Cycloheptane	g	—	−28.520	15.060	81.82	—	—	—	—	—	—	—	—
		lq	—	−37.730	12.980	57.97	43.20	—	—	—	—	—	—	—
C_7H_{14}	Methylcyclo-hexane	g	1099.59	−36.990	6.52	82.06	32.27	—	—	—	—	572.1	34.3	0.251
		lq	—	−45.450	4.86	59.26	43.80	—	—	—	—	—	—	—
C_7H_{14}	1-Heptene	g	1121.690	−14.890	22.950	101.24	37.10	2.344	144.802	−79.864	298-1500	—	—	—
		lq	—	−25.380	19.200	81.31	50.62	—	—	—	—	—	—	—
C_7H_{16}	n-Heptane	g	1160.010	−44.890	1.940	102.24	39.67	1.200	156.252	−83.35	298-1500	540.2	27	0.259
		lq	—	−53.630	0.270	78.52	33.2	33.2	—	—	—	—	—	—
C_8H_8	Styrene (vinyl-benzene)	g	1060.900	35.110	51.100	82.48	29.18	−3.13	130.4	−52.9	298-1000	—	—	—
		lq	—	24.830	48.370	56.78	43.64	—	—	—	298	—	—	—
C_8H_{10}	Ethylbenzene	g	1103.130	7.120	31.208	86.15	30.69	−8.266	158.029	−97.963	298-1000	619.6	37	0.272
		lq	—	−2.977	28.173	60.99	44.56	—	—	—	—	—	—	—
C_8H_{10}	1,2-Dimethyl-benzene (o-xylene)	g	1098.540	4.540	29.177	84.31	31.85	−3.54	141.285	−81.164	298-1500	632.2	36	0.254
		lq	—	−5.841	26.370	58.91	44.9	44.9	—	—	298	—	—	—
C_8H_{10}	1,3-Dimethyl-benzene (m-xylene)	g	1098.120	4.120	28.405	85.49	30.49	−6.545	148.393	−86.973	298-1500	619.2	35	0.258
		lq	—	−6.075	25.730	60.25	43.8	43.8	—	—	298	—	—	—

Formula	Compound	State												
C_8H_{10}	1,4-Dimethylbenzene (p-xylene)	g	1098.290	4.290	28.952	84.23	30.32	−6.196	145.716	−83.786	298-1500	618.2	34	0.252
		lq	—	−5.838	26.310	59.12	43.9	43.9	—	—	298	—	—	—
C_8H_{16}	1-Octene	g	1279.130	−49.820	3.950	111.55	45.14	2.906	165.463	−91.073	298-1000	578.0	25.5	0.254
		lq	—	−59.740	1.580	86.23	60.74	60.74	—	—	298	—	—	—
C_8H_{18}	n-Octane	g	1317.450	−49.820	3.950	111.55	45.14	1.651	177.317	−94.95	298-1500	569.9	24.6	0.256
		lq	—	−59.740	1.580	86.23	60.74	—	—	—	—	—	—	—
C_8H_{18}	2,2,4-Trimethylpentane (isooctane)	g	—	−53.570	3.270	101.15	—	—	—	—	—	544.3	25.5	0.274
		lq	1313.690	−61.970	1.650	78.40	57.2	—	—	—	—	—	—	—
C_9H_{12}	n-Propylbenzene	g	1258.240	1.870	32.810	95.74	36.73	−7.158	177.359	−108.098	298-1000	638.8	32	0.262
		lq	—	−9.178	29.600	89.44	—	—	—	—	—	—	—	—
C_9H_{12}	Isopropylbenzene (cumene)	g	1257.310	0.940	32.738	92.87	36.26	−9.179	184.622	−115.437	298-1000	635.9	32	0.263
		lq	—	−9.848	29.708	66.87	—	—	—	—	—	—	—	—
C_9H_{12}	1,2,4-Trimethylbenzene (pseudocumene)	g	1253.040	−3.330	29.969	94.54	36.81	—	—	—	—	649.0	32	0.258
		lq	—	−14.785	24.507	67.73	51.38	—	—	—	—	—	—	—
C_9H_{20}	n-Nonane	g	1479.900	−54.740	5.960	120.86	50.60	2.086	138.317	116.53	298-1000	595.2	22.5	0.250
		lq	—	−65.840	3.840	94.09	67.97	—	—	—	—	—	—	—
$C_{10}H_8$	Naphthalene	g	—	36.330	53.630	80.43	32.08	39.9	—	—	—	748.2	40.6	—
		c	1232.500	18.750	48.100	40.01	39.9	39.9	—	—	298	—	—	—
$C_{10}H_{14}$	n-Butylbenzene	g	1415.440	−3.300	34.580	105.04	42.42	−6.911	199.087	−120.368	298-1000	661.3	28.4	0.257
		lq	—	−15.280	30.990	76.9	57.4	—	—	—	—	—	—	—
$C_{10}H_{18}$	cis-Decalin	g	—	−40.380	20.510	90.28	39.84	—	—	—	—	691.7	28.6	0.267
		lq	1052.500	−52.450	16.470	63.34	55.45	—	—	—	—	—	—	—
$C_{10}H_{18}$	trans-Decalin	g	1499.500	−43.570	17.550	89.52	40.04	—	—	—	—	681.5	28.7	0.267
		lq	—	−55.140	13.790	63.32	54.61	—	—	—	—	—	—	—
$C_{10}H_{22}$	n-Decane	g	1632.340	−59.670	7.970	130.17	56.07	2.521	159.613	120.356	298-1000	617.2	20.8	0.247
		lq	—	−71.950	4.120	101.79	75.16	—	—	—	—	—	—	—
$C_{11}H_{24}$	n-Undecane	g	1789.789	−64.600	9.980	139.31	61.53	2.956	180.817	130.05	298-1000	640.2	19.2	0.241
		lq	—	−78.060	5.420	109.50	62.47	—	—	—	—	—	—	—

Molecular formula	Name	State	$-(\Delta H^\circ_{298})_{comb}$	$(\Delta H^\circ_{298})_{form}$	$(\Delta G^\circ_{298})_{form}$	S°_{298}	$(C^\circ_p)_{298}$	a	$b\times10^3$	$c\times10^6$	Temperature interval, K	T_{cr}	p_{cr}	z_{cr}
$C_{12}H_{10}$	Diphenyl	g	—	41.300	67.860	83.3	—	—	—	—	—	768.8	31.8	0.257
		lq	—	23.100	39.830	49.7	—	—	—	—	—	—	—	—
		c	1493.600	24.530	61.260	49.2	47.1	47.1	—	—	298	—	—	—
$C_{12}H_{26}$	n-Dodecane	g	1947.230	—68.520	11.980	148.79	67.00	3.391	201.917	141.75	298-1000	659.2	17.9	0.238
		lq	—	—84.160	6.710	117.27	89.86	—	—	—	—	—	—	—
$C_{13}H_{12}$	Diphenylmeth-ane	lq	1615.400 c	21.25	66.190	57.2	55.7	—	—	—	—	770.2	28.2	—
$C_{13}H_{28}$	n-Tridecane	g	2104.670	—74.450	13.990	158.09	72.47	3.726	223.317	153.45	298-1000	677.2	17	0.239
		lq	—	—90.270	8.030	124.97	97.25	—	—	—	—	—	—	—
$C_{14}H_{10}$	Anthracene	c	1700.400	25.530	62.950	49.6	49.7	49.7	—	—	298	—	—	—
$C_{14}H_{10}$	Phenanthrene	c	1692.500	26.650	63.770	50.6	56.0	56.0	—	—	298	—	—	—
$C_{14}H_{30}$	n-Tetradecane	g	2262.110	—79.380	16.000	167.40	77.93	4.263	304.19	—165.51	298-1000	695.2	16	0.233
		lq	—	—98.380	9.300	132.75	104.79	—	—	—	—	—	—	—
$C_{15}H_{32}$	n-Pentadecane	g	2419.550	—84.310	18.010	176.71	83.40	4.701	265.517	176.85	298-1000	710.2	15	0.229
		lq	—	—102.490	10.630	140.42	112.32	—	—	—	—	—	—	—
$C_{16}H_{34}$	n-Hexadecane	g	2577.000	—89.230	20.020	186.02	88.86	5.131	286.517	188.55	298-1000	717.0	14	0.226
		lq	—	—108.580	11.950	148.10	119.85	—	—	—	—	—	—	—
$C_{17}H_{36}$	n-Heptadecane	g	2734.440	—94.150	22.030	195.53	94.33	5.571	307.817	199.95	298-1000	736.2	13	0.216
		lq	—	—114.690	11.950	148.10	—	—	—	—	—	—	—	—
$C_{18}H_{38}$	n-Octadecane	g	2891.880	—99.080	24.040	204.64	99.80	6.001	328.797	211.98	298-1000	756.2	13	0.230
		lq	—	—120.800	13.670	166.5	—	—	—	—	—	—	—	—
		c	—	—135.920	12.800	118.7	—	—	—	—	—	—	—	—

Formula	Compound	State												
C₁₉H₄₀	n-Nonadecane	g	3049.330	−104.000	26.050	213.95	105.26	6.431	352.317	223.45	298-1000	760.2	12	0.212
C₂₀H₄₂	n-Eicosane	g	3206.770	−108.930	28.060	223.26	110.73	6.875	431.064	−235.353	298-1000	775.2	11	0.208
		lq	—	−133.010	—	—	—	—	—	—	—	—	—	—
	(b) Alcohols, Ethers, Esters, Aldehydes, Ketones, Acids													
CH₂O	Formaldehyde	g	134.100	−27.770	−26.300	52.6	8.45	4.498	13.953	−3.73	291-1500	—	—	—
CH₂O₂	Formic acid	g	—	−86.670	−80.240	60.0	13.0	7.33	21.32	−8.255	300-700	—	—	—
		lq	62.800	−97.800	−82.700	30.82	23.67	23.67	24.78	—	298	—	—	—
CH₄O	Methanol	g	170.900	−48.080	−38.690	56.8	11.8	4.88	—	−5.889	300-700	513.2	78.5	0.222
		lq	—	−57.020	−39.730	30.3	19.5	19.5	—	—	298	—	—	—
C₂H₄O	Acetaldehyde	g	280.000	−39.760	−31.960	63.5	15.0	7.422	29.029	−8.742	298-1500	461.2	54.7	0.257
C₂H₄O	Ethylene oxide	g	279.00	−12.190	−2.790	58.1	11.5	—	—	—	—	468.2	71.0	0.255
C₂H₄O₂	Acetic acid	g	—	−104.300	−91.200	70.1	11.3	5.20	46.16	−18.35	300-700	594.8	57.1	0.260
		lq	209.400	−116.400	−93.800	38.2	29.5	13.10	55	—	297-353	—	—	—
C₂H₄O₂	Methyl formate	g	—	−83.600	−69.080	65.458	—	—	—	—	—	487.2	59.2	0.255
		lq	—	−90.400	—	—	29.0	—	—	—	—	—	—	—
C₂H₆O	Ethanol	g	327.600	−56.240	−40.300	67.4	17.0	4.946	49.087	−23.885	300-1500	516.2	63.0	0.248
		lq	—	−66.356	−41.770	38.4	26.64	25.46	−39.6	137.0	283-348	—	—	—
C₂H₆O₂	Ethylene glycol	g	281.900	−92.800	−71.520	77.33	18.8	—	—	—	—	—	—	—
		lq	—	−108.580	−77.140	39.9	35.7	—	—	—	—	—	—	—
C₃H₆O	Acetone	g	426.800	−51.790	−36.400	70.72	29.81	5.371	48.227	−15.182	298-1500	508.7	46.6	0.237
		lq	—	−59.340	−37.150	47.8	18.0	13.29	55.5	—	298-320	—	—	—
C₃H₈O	Propanol	g	480.500	−62.220	−39.509	77.25	31.35	—	—	—	—	537.2	50.2	0.252
		lq	—	−73.370	−41.370	46.1	18.4	—	—	—	—	—	—	—
C₃H₈O	Isopropanol	g	—	−65.560	−42.210	75.1	39.4	—	—	—	300-1500	508.8	47	0.248
		lq	474.800	−76.180	−43.260	43.0	35.9	—	—	—	—	—	—	—
C₃H₈O	Glycerine	lq	397.000	−159.800	−114.015	48.87	—	—	—	—	—	—	—	—
C₄H₈O	Methyl-ethyl ketone	g	—	−58.300	—	—	38.5	—	—	—	—	535.2	41.0	0.249
		lq	—	−66.600	−37.710	57.7	—	—	—	—	—	—	—	—
C₄H₈O₂	1,4-Dioxane	g	—	−85.470	—	—	36.5	—	—	—	—	588.2	51.4	0.253
		lq	536.900	−95.080	−55.630	47.0	36.5	36.5	—	—	298	—	—	—

Molecular formula	Name	State	$-(\Delta H°_{298})_{comb}$	$(\Delta H°_{298})_{form}$	$(\Delta G°_{298})_{form}$	$S°_{298}$	$(C°_p)_{298}$	Heat capacity — Coefficients of equation $C°_p = f(T)$			Temperature interval, K	T_{cr}	p_{cr}	z_{cr}
								a	$b×10^3$	$c×10^6$				
C$_4$H$_8$O$_2$	Butyric acid	lq	520.000	−128.080	−90.750	54.1	42.1	—	—	—	—	628.2	52	0.293
C$_4$H$_8$O$_2$	Ethyl acetate	g	—	−103.444	−78.860	90.11	—	—	—	—	—	523.3	37.8	0.252
		lq	536.900	−112.570	−77.600	62.0	40.4	—	—	—	—	—	—	—
C$_4$H$_8$O$_2$	n-Butyl alcohol	g	—	−67.540	−39.090	89.42	—	—	—	—	—	563.2	43.6	0.259
		lq	638.600	−79.340	−40.130	54.5	43.8	—	—	—	—	—	—	—
C$_4$H$_{10}$O	Tertiary butyl alcohol	g	—	−77.590	—	45.3	—	—	—	—	—	506.2	39.2	0.259
		lq	629.300	−88.690	−46.740	—	53.8	—	—	—	—	—	—	—
C$_4$H$_{10}$O	Diethyl ether	g	—	−59.700	−28.090	84.4	—	—	—	—	—	467.2	35.6	0.255
		lq	651.700	−65.300	−27.880	60.5	40.8	—	—	—	—	—	—	—
C$_5$H$_{12}$O	n-Amyl alcohol	g	—	−73.410	—	—	—	—	—	—	—	583	37.4	0.260
		lq	793.700	−85.860	−38.850	60.9	50.0	—	—	—	—	—	—	—
C$_6$H$_4$O$_2$	n-Benzoquinone	c	—	−44.100	−20.000	38.9	31.7	5.4	89.0	—	73-298	—	—	—
C$_6$H$_6$O	Phenol	g	—	−22.500	−8.220	78.5	23.7	—	—	—	—	694.4	60.5	0.244
		c	732.200	−37.260	−9.740	34.0	31.8	—	—	—	—	—	—	—
C$_6$H$_6$O$_2$	Hydroquinone	c	683.700	−86.750	−49.480	33.50	33.40	5.5	68.8	52.0	78-296	—	—	—
C$_6$H$_{12}$O	Cyclohexanol	lq	890.700	−83.450	−32.070	47.70	49.93	2.0	102.0	—	187-445	—	—	—
C$_6$H$_{14}$O	n-Hexyl alcohol	g	—	−78.920	—	—	—	—	—	—	—	611	40	—
		lq	—	−91.970	−37.550	68.6	55.57	—	—	—	—	—	—	—
C$_7$H$_6$O$_2$	Benzoic acid	c	771.200	−91.910	−58.700	40.8	34.7	—	—	—	—	—	—	—
C$_7$H$_{16}$O	n-Heptyl alcohol	lq	1104.900	−97.220	−35.850	77.9	—	—	—	—	—	640	29.4	—
C$_8$H$_6$O$_4$	o-Phthalic acid	c	771.000	−186.880	−141.320	49.7	45.0	—	—	—	—	—	—	—
C$_8$H$_{18}$O	n-Octyl alcohol	g	—	−89.660	—	—	—	—	—	—	—	660	26.5	—
		lq	—	−103.610	−34.350	84.0	—	—	—	—	—	—	—	—
C$_{12}$H$_{10}$O$_4$	Quinhydrone	c	—	−19.790	−77.190	77.9	66.2	—	—	—	—	—	—	—

(c) Halogen Derivatives

Formula	Name	State												
$C_{16}H_{34}O$	Cetyl alcohol	lq	—	−151.730	−22.97	145.0	—	—	—	—	—	—	—	—
		c	2504.500	−163.420	−23.620	108.0	—	—	—	—	—	—	—	—
CF_4	Carbon tetrafluoride	g	—	−218.000	−207.270	62.48	14.61	—	—	—	—	227.2	41.4	—
CCl_4	Carbon tetrachloride	g	44.500	−25.500	−15.300	73.95	19.96	23.34	2.30	—	298-1000	536.4	45.0	—
		lq	37.300	−33.300	−16.400	51.25	31.49	23.42	36.70	—	273-330	—	—	—
$CClF_3$	Chlorotrifluoromethane	g	—	−171.000	−161.300	68.23	15.97	—	—	—	—	342.0	39.0	0.278
CCl_2F_2	Dichlorodifluoromethane	g	—	−112.000	−102.650	71.84	17.28	—	—	—	—	384.7	39.6	0.273
CCl_3F	Trichlorofluoromethane	g	—	−70.000	−60.580	73.96	18.61	—	—	—	—	471.2	43.2	0.277
CH_3Cl	Methyl chloride	g	164.200	−20.630	−14.960	55.80	9.73	3.562	23.0	−7.541	273-800	416.3	65.9	0.276
CH_3I	Methyl iodide	g	193.700lq	4.900	5.300	60.85	10.55	4.105	24.487	−9.733	298-600	528.2	72.7	—
CH_2Cl_2	Dichloromethane	g	106.800	−21.000	−14.000	64.68	12.28	8.000	15.6	—	273-800	510.2	60	—
$CHCl_3$	Chloroform	g	96.250	−24.000	−16.000	70.86	15.73	7.052	35.598	−21.68	273-800	536.6	54	0.294
		lq	89.200	−31.500	−17.100	48.5	27.8	—	—	—	—	—	—	—
$C_2H_4Cl_2$	1,2-Dichloroethane	g	271.000	−31.300	−18.000	73.81	19.0	—	—	—	—	561.0	53	0.259
		lq	—	−39.600	−20.200	49.84	—	—	—	—	—	—	—	—
$C_2H_4Br_2$	1,2-Dibromoethane	g	—	−9.300	−2.520	78.81	—	—	—	—	—	553	70.6	—
		lq	—	−19.300	−4.940	53.37	32.51	—	—	—	—	—	—	—
C_2H_5Cl	Ethyl chloride	g	316.700	−25.700	−13.260	65.68	14.90	—	—	—	—	464.4	52	—
C_3H_7Cl	Isopropyl chloride	g	—	−34.560	−14.920	74.10	20.93	—	—	—	—	503.2	45.2	—
C_6Cl_6	Hexachlorobenzene	c	—	−31.300	0.300	62.20	48.11	—	—	—	—	—	—	—
C_6Cl_5OH	Pentachlorophenol	c	—	−70.600	−34.400	60.21	48.27	—	—	—	—	—	—	—
C_6H_5F	Fluorobenzene	g	—	−26.480	−15.100	72.33	22.57	—	—	—	—	560.1	44.9	0.263
		lq	—	−34.750	−16.500	49.22	—	—	—	—	—	—	—	—

Molecular formula	Name	state	$-(\Delta H^\circ_{298})_{comb}$	$(\Delta H^\circ_{298})_{form}$	$(\Delta G^\circ_{298})_{form}$	S°_{298}	$(C^\circ_p)_{298}$	a	$b\times10^3$	$c\times10^6$	Temperature interval, K	T_{cr}	p_{cr}	z_{cr}
C_6H_5Cl	Chlorobenzene	g	—	12.210	23.530	74.86	23.20	—	—	—	—	632.4	44.6	0.265
		lq	—	2.550	22.120	47.2	35.9	—	—	—	—	—	—	—
C_6H_5Br	Bromobenzene	g	—	21.620	29.560	77.76	23.83	—	—	—	—	670.2	44.6	0.263
		lq	—	11.600	27.820	49.7	37.17	—	—	—	—	—	—	—
C_6H_5I	Iodobenzene	g	—	—	—	79.85	24.08	—	—	—	—	721.2	44.6	0.265
		lq	—	27.400	—	49.10	37.95	—	—	—	—	—	—	—

(d) Nitrogen and Sulphur Derivatives

Molecular formula	Name	state	$-(\Delta H^\circ_{298})_{comb}$	$(\Delta H^\circ_{298})_{form}$	$(\Delta G^\circ_{298})_{form}$	S°_{298}	$(C^\circ_p)_{298}$	a	$b\times10^3$	$c\times10^6$	Temperature interval, K	T_{cr}	p_{cr}	z_{cr}
CH_3NO_2	Nitromethane	g	—	−17.860	−1.66	65.73	—	—	—	—	—	588.2	62.3	0.223
		lq	169.400	−27.030	−3.480	41.1	25.3	—	—	—	—	—	—	—
CH_3NO_3	Methyl nitrate	g	—	−29.400	—	51.86	37.57	—	—	—	—	—	—	—
		lq	—	−37.200	−9.500	—	—	—	—	—	—	—	—	—
CH_4N_2O	Carbamide	c	151.600	−79.634	−47.120	25.00	22.26	—	—	—	—	—	—	—
CH_5N	Methylamine	g	256.100 lq	−6.700	6.600	57.73	12.9	—	—	—	—	430.1	73.6	—
C_2N_2	Dicyanogen	g	—	73.600	70.810	57.86	13.60	—	—	—	—	400.0	50.0	—
C_2H_3N	Methylcyanide	g	—	21.000	25.300	58.01	12.40	—	—	—	—	—	—	—
		lq	302.400	12.700	24.000	34.5	—	—	—	—	—	—	—	—
$C_2H_5NO_2$	Glycine (glycol)	c	234.500	−126.300	−88.600	26.10	24.00	—	—	—	—	—	—	—
C_2H_7N	Dimethylamine	g	—	−6.600	14.100	65.3	—	—	—	—	—	456.2	55.5	0.280
		lq	416.700	−13.900	13.910	43.58	16.58	—	—	—	—	—	—	—
$C_3H_6N_6$	Melamine	g	—	−17.130	42.330	35.63	—	—	—	—	—	—	—	—

Formula	Compound	State												
C$_3$H$_9$N	Trimethyl-amine	lq	578.600	10.900	45.960	49.82	32.00	—	—	—	—	433.3	40.2	0.287
C$_4$H$_4$S	Thiophene	g	—	27.490	34.780	66.65	17.42	—	—	—	—	580.1	56.2	—
		lq	—	19.200	28.800	43.30	—	—	—	—	—	—	—	—
C$_4$H$_9$N$_3$O$_2$	Creatine	c	—	−128.420	−63.350	45.3	—	—	—	—	—	—	—	—
C$_5$H$_5$N	Pyridine	g	—	33.500	45.470	67.59	18.67	—	—	—	—	617.4	60.0	—
		lq	658.500	23.890	43.330	42.52	31.72	—	—	—	—	—	—	—
C$_5$H$_6$S	2-Methyl thiophene	g	—	15.600	24.970	76.62	22.80	—	—	—	—	—	—	—
		lq	—	10.860	27.510	52.22	—	—	—	—	—	—	—	—
C$_5$H$_6$S	3-Methyl thiophene	g	—	19.940	29.260	76.79	22.67	—	—	—	—	—	—	—
		lq	—	10.490	27.150	52.18	—	—	—	—	—	—	—	—
C$_6$H$_5$NO$_2$	Nitrobenzene	lq	739.200	3.800	34.950	53.6	44.4	—	—	—	—	—	—	—
		g	—	15.480	—	—	—	—	—	—	—	—	—	—
C$_6$H$_6$N$_2$O$_2$	o-Nitroaniline	c	—	−3.450	42.600	42.1	39.3	—	—	—	—	—	—	—
C$_6$H$_6$N$_2$O$_2$	m-Nitroaniline	c	—	−4.460	41.600	42.1	40.2	—	—	—	—	—	—	—
C$_6$H$_6$N$_2$O$_2$	p-Nitroaniline	c	—	−9.920	36.100	42.1	40.4	—	—	—	—	—	—	—
C$_6$H$_6$S	Thiophenol	g	—	26.660	35.280	80.51	25.07	—	—	—	—	—	—	—
		lq	—	15.020	31.770	53.25	41.40	—	—	—	—	—	—	—
C$_6$H$_7$N	Aniline	g	—	20.900	—	45.8	47.7	80.85	−255.4	483.3	278−348	699.2	52.4	0.250
		lq	811.700	8.440	36.620	45.8	—	—	—	—	—	—	—	—
C$_6$H$_{11}$NO	e-Caprolactam	c	—	−78.450	−22.720	40.3	—	—	—	—	—	—	—	—
C$_7$H$_{13}$NO	α-Enantholactam	c	—	−83.020	−19.100	45.4	—	—	—	—	—	—	—	—
C$_9$H$_7$N	Quinoline	lq	—	37.300	65.900	51.9	—	—	—	—	—	—	—	—
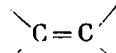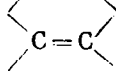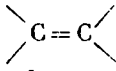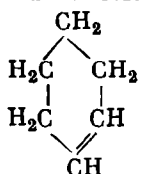
2. Numerical Values of the Thermal Characteristic x of Konovalov's Equation [7, 8]

Group of atoms and kind of bond	x, kcal/mol	x, kJ/mol
Single bond C—C	0	0
Double bond C=C	21	87.86
Triple bond C≡C	51	213.38
Phenyl group R—C$_6$H$_5$	24	100.41
Alcohol group R—CH$_2$OH	12	50.21
Ethers R—O—R	21	87.86
Aldehyde group R—CHO	18	75.31
Ketone group R—CO—R	12	50.21
Acid group in monobasic acid R—COOH	0	0
Acid group in dibasic acid HOOC—R—COOH	3	12.55
Alkylcyclohexanes $$R-HC\begin{array}{c} CH_2-CH_2 \\ \diagup \qquad \diagdown CH_2 \\ CH_2-CH_2 \end{array}$$	0	0
Alkylcyclopentanes $$R-HC\begin{array}{c} CH_2-CH_2 \\ \diagup \qquad \mid \\ CH_2-CH_2 \end{array}$$	6	25.10

3. Heat Corrections for the Kharasch Equation [37, 7]
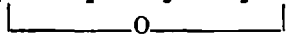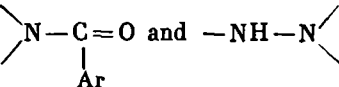
Nature of groups, substituents, and bonds	Heat correction Δ_i, kcal/mol	Remarks
Bond between aliphatic and aromatic radicals Alk—Ar	3.5	Upon combustion of the carbon atoms, one ·of which belongs to an aromatic and the other to an aliphatic radical, all the electrons belonging to these atoms will migrate; $p=0$
Bond between aromatic radicals Ar—Ar	6.5	Upon combustion, all the electrons belonging to the carbon atoms migrate. The number of structural heat corrections for polycyclic compounds equals the number of "junctions" of the nuclei

Nature of groups, substituents, and bonds	Heat correction Δ_i, kcal/mol	Remarks
Double bond $\diagdown\text{C} = \text{C}\diagup$	−13.0	
Double bond $\diagup\text{C} = \text{C}\diagup$ in *cis*-compounds	−16.5	
Double bond $\diagdown\text{C} = \text{C}\diagup$ in *trans*-compounds	−13.0	
Bond between aromatic radical and vinyl $Ar-CH = CH_2$ or acetyl $Ar-C\equiv CH$ radicals	6.5	
Double bond in closed ring CH_2 H_2C CH_2 H_2C CH CH	−6.5	
Triple bond $-C \equiv CH$	−46.1	
Group $-C \equiv C-$ not bound to hydrogen	−33.1	
Bond between primary aliphatic radical and hydroxyl group (primary alcohol)	−13	Upon combustion of the carbon bound to a hydroxyl group, only three and not all of the electrons migrate. The electron participating in the formation of a bond between carbon and oxygen, and also that of the hydrogen in the hydroxyl group do not migrate; $p = 2$
Bond between secondary aliphatic radical and hydroxyl group (secondary alcohol)	−6.5	Ditto
Bond between tertiary aliphatic radical and hydroxyl group (tertiary alcohol)	−3.5	Ditto
Bond between aromatic radical and hydroxyl group	−3.5	The same as for aliphatic alcohols

Nature of groups, substituents, and bonds	Heat correction Δ_i, kcal/mol	Remarks
Aliphatic and aromatic ethers Alk (Ar) — O — (Ar) Alk	−19.5	Only two electrons of the carbon bound to the oxygen migrate upon combustion; $p=2$
Aliphatic esters $$Alk - \overset{\displaystyle O}{\overset{\displaystyle \parallel}{C}} - O - Alk$$	−16.5	$p=4$
Aldehyde group in aliphatic and aromatic compounds	−13	In the aldehyde group, two electrons of the carbon bound to the oxygen migrate upon combustion; $p=2$
Ketone group in aliphatic and aromatic compounds	−6.5	Ditto
α-Keto-acids $R - C \overset{\nearrow O}{\underset{\searrow COOH}{}}$	−13	If the radical $R - \overset{\mid}{C} = O$ is bound to the group —COOH, the indicated correction is introduced for this bond; in general the group —COOH does not require such a correction. Upon combustion, only one of the electrons belonging to the carbon of the carboxyl group migrates
Hydroxy-acids $\overset{\searrow}{\underset{\nearrow}{}} C \overset{\nearrow COOH}{\underset{\searrow OH}{}}$	−6.5	The correction is introduced only in case of a bond of the radical $\overset{\searrow}{\underset{\nearrow}{}} C(OH)$ to the group —COOH. For the remaining cases see α-keto-acids
Group $R - \overset{\parallel}{\underset{O}{C}} - \overset{\parallel}{\underset{O}{C}} - R$	−13	The correction is introduced only if the radical $R - \overset{\parallel}{\underset{O}{C}} -$ is bound to a similar one
Trimethylene rings in carboxylic acids $$\overset{\mid}{\underset{\mid}{\overset{\displaystyle -C}{\underset{\displaystyle -C}{}}}} \overset{\diagdown}{\underset{\diagup}{C}} \overset{\diagup}{\underset{\diagdown COOH}{}}$$	−13	

Nature of groups, substituents, and bonds	Heat correction Δ_i, kcal/mol	Remarks
Cyclobutane rings in carboxylic acids $-\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$ $-\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-COOH$	-13	
Lactones of the type $H_2C-CH_2-CH_2-CH_2-C=O$ $\underset{\rule{1.5cm}{0.4pt}}{\mid}\quad O\quad\underset{\rule{1.5cm}{0.4pt}}{\mid}$	-13	
Carboxylic acid anhydrides	-10	
Primary aliphatic amines $Alk-NH_2$	-13	Upon combustion, all the electrons belonging to the carbon bound to the aminogroup migrate. When calculating the number of migrating electrons, the electrons belonging to the hydrogen directly bound to the nitrogen are also taken into account
Secondary aliphatic amines $Alk-NH-Alk$	-19.5	Ditto
Tertiary aliphatic amines $Alk-\overset{\mid}{\underset{\mid}{N}}-Alk$ Alk	-26	Ditto
Primary aromatic amines $Ar-NH_2$	-6.5	Ditto
Secondary aromatic amines $Ar-NH-Ar$	-13	Ditto
Tertiary aromatic amines $Ar-\overset{\mid}{\underset{\mid}{N}}-Ar$ Ar	-19.5	Ditto. Fatty-aromatic tertiary amines are considered tertiary aromatic
Substituted amines of the type $\diagdown N-C=O$ and $-NH-N\diagup$ $\quad\ \overset{\mid}{Ar}$	-6.5	
Acetylated aromatic amines $Ar-NH-C=O$ $\qquad\overset{\mid}{CH_3}$	3.5	

Nature of groups, substituents, and bonds	Heat correction Δ_i, kcal/mol	Remarks
Bond between carbon and the nitrile group $-C \equiv N$ in aliphatic and aromatic compounds	−16.5	Upon combustion, all four electrons of the carbon bound to the nitrogen in the nitrile group migrate
Aromatic nitriles	6.5	Two corrections are introduced when calculating ΔH_{comb}: for the bond between carbon and the group $-C \equiv N$ and to take into account the presence of the nitrile group itself
Isonitrile group $Alk-N = C\diagdown^{\diagup}$ in an aliphatic series	−33.1	
Nitrogroup $-NO_2$ in aliphatic and aromatic compounds	−13	Upon combustion, all but one of the electrons of the carbon bound to the nitrogroup migrate; this electron remains with the nitrogen of the nitrogroup which is reduced in the process of combustion; $p = 1$
Chlorine in aliphatic compounds $Alk-Cl$	−13	$p = 1$
Bromine in aromatic compounds $Ar-Br$	−13	$p = 1$
Chlorine in aromatic compounds $Ar-Cl$	−6.5	Upon combustion of halogen-containing compounds, all but one of the electrons of the carbon atom bound to the halogen migrate; $p = 1$
Bromine in aliphatic compounds $Alk-Br$	−13	Ditto
Iodine in aromatic compounds $Ar-I$	−40.1	Ditto
Iodine in aliphatic compounds $Alk-I$	−40.1	Ditto
Sulphogroup in aliphatic compounds $Alk-SO_3H$	23.4	
Quinones	−33.1	

4. Numerical Values of Constants (kcal/mol)
Used to Calculate the Standard Heats of Combustion and Formation
of Alkanes from Simple Substances at 298.15 K
According to Tatevsky [40]

Bond	Symbol	$-(\Delta H^{\circ}_{298})^{g}_{comb}$	$-(\Delta H^{\circ}_{298})^{lq}_{comb}$	$-(\Delta H^{\circ}_{298})^{g}_{form}$
$C_1 - C_2$	$A_{1,2}$	265.17	263.24	12.54
$C_1 - C_3$	$A_{1,3}$	228.48	226.99	10.79
$C_1 - C_4$	$A_{1,4}$	210.01	208.68	10.03
$C_2 - C_2$	$A_{2,2}$	157.41	156.23	4.96
$C_2 - C_3$	$A_{2,3}$	121.35	120.45	2.58
$C_2 - C_4$	$A_{2,4}$	103.35	102.70	1.35
$C_3 - C_3$	$A_{3,3}$	86.45	85.55	−0.98
$C_3 - C_4$	$A_{3,4}$	69.40	68.90	−3.14
$C_4 - C_4$	$A_{4,4}$	53.22	(57.77)*	−6.19

* The value is not accurate, because owing to the absence of other experimental data it has been determined from the value of $(\Delta H^{\circ}_{298})^{lq}_{comb}$ for only one alkane.

5. Contributions of Selected Bonds and Atomic Groups
to Standard Heats of Combustion and Formation
from Simple Substances at 298.15 K for Organic Compounds
in the Gaseous and Liquid States According to Laidler [41, 42]

Bond (or group)	Symbol	$-(\Delta H^{\circ}_{298})_{comb},$ kcal/mol		$(\Delta H^{\circ}_{298})_{form},$ kcal/mol	
		gas	liquid	gas	liquid
$C - C$	c	47.48	47.48	−0.45	−0.45
$C = C$	c_2	32.50	(32.50)	30.20	(30.20)
$C \equiv C$	c_3	196.30	(196.30)	55.30	(55.30)
	p	54.22	53.73	3.45	3.95
	s	55.04	54.46	2.64	3.21
	t	55.89	55.37	1.78	2.30
	p'	53.79	(53.29)	−3.89	(−4.38)
$C - H$	s'	54.69	(54.11)	2.99	(3.57)
	t'	55.20	(54.69)	2.47	(2.99)
	p_2	75.58	(75.00)	−10.07	(−9.49)
	s_2	98.87	(98.45)	−25.62	(−24.11)
	t_3	56.39	(55.87)	1.29	(1.80)
$C - O - H$		13.75	6.99	49.93	50.69
$C - O - C$		20.00	18.70	27.00	28.30
$C - CHO$		122.20	117.00	29.50	34.70
$C - CO - C$		107.70	100.9	33.40	40.20

Bond (or group)	Symbol	$-(\Delta H^{\circ}_{298})_{comb}$ kcal/mol		$(\Delta H^{\circ}_{298})_{form}$ kcal/mol	
		gas	liquid	gas	liquid
C—COOH		56.70	37.90	95.10	113.90
C—NH$_2$		95.30	—	—3.50	—
C—NO$_2$		12.60	5.50	11.00	18.00
C—ONO$_2$		2.40	—4.00	21.10	27.50
C—NHNO$_2$		—	56.80	—	0.90
$\begin{matrix} C \\ \diagdown \\ \diagup \\ C \end{matrix} N—NO_2$		—	55.90	—	8.90

6. Bond Energies [7, 8, 18, 19]

Bond	ε, kcal	Bond	ε, kcal
H—H	103.2	C=O (in HCHO)	144
H—C	85.6	C=O (in other alde-	~ 150
H—N (in NH$_3$)	83.3	hydes)	
H—O	110.0	C=O (in ketones)	156
H—F	134	C=O (in CO)	~ 224
H—P	63.0	C=O (in CO$_2$)	168
H—S	82	C=O (in HCOOH)	348
H—Cl	102.1	$\diagdown$ OH	
H—Br	85.9	C=O (in other acids)	~ 360
H—I	70.6		
Sublimation of carbon	~ 125	$\diagdown$ OH	
(diamond and graphite)	171.3 [43]	C=O (in formates)	313
C—C	62.8	$\diagdown$ OC	
	85.0 [43]		
C=C	101.2	C=O (in other esters)	327
C≡C (acetylene)	128.2	$\diagdown$ OC	
C—N	53.5		
C=N	~ 84	C—F	104
C≡N (in HCN)	146	C—Si	57.6
C≡N (in nitriles)	149	C—S	54
C≡N (in isonitriles)	139	C=S (in CS$_2$)	117.5
C—O (in alcohols)	75	C—Cl	70
C—O (in ethers)	75	C—Br	57

Bond	ε, kcal	Bond	ε, kcal
C — I	43	S = S	~ 101
N — N	~ 27	F — F	~ 37
N = N	~ 80	Cl — Cl	57.2
N $\equiv$ N	170.2	Cl — Br	52.7
N — O	~ 61	Cl — I	51.0
N = O	108	Br — Br	45.54
N = O (in NO)	149.6	Br — I	42.9
N = O	169-186	I — I	35.6
$\diagdown$O		Na — Na	17.8
		K — K	11.8
N — Cl	38.4	Na — Cl	97.5
O = O	117.2	Na — Br	87.7
O — Cl	49.3	Si — O	101.5
P $\equiv$ P	116	B — C	70
S — Cl	57.2	Sublimation of iodine	14.88
S = O	92.2	$[I_2(c) \rightarrow I_2(g)]$	
S — S	102.6		

7. *Corrections for Approximate Calculation of Standard Heats
of Formation from Simple Substances, Heat Capacities, and Entropies
(in Idealized Gaseous State) by the Method of Introducing Corrections
for the Substitution of Hydrogen by* —CH₃ *and Other Groups* [44, 45]

(a) *Properties of Basic Groups*

Substance	$(\Delta H^{\circ}_{298})_{form}$, kcal/mol	S°_{298}, cal/mol·K	Coefficients of equation $C^{\circ}_p = \varphi(T)$ (C°_p is in cal/mol·K)		
			a	$b \times 10^3$	$c \times 10^6$
Methane	−17.89	44.50	3.79	16.62	−3.24
Cyclopentane	−18.46	70.00	−9.02	109.28	−40.23
Cyclohexane	−29.43	71.28	−11.53	139.65	−52.02
Benzene	19.82	64.34	−4.20	91.30	−36.63
Naphthalene	35.40	80.70	3.15	109.40	−34.79
Methylamine	−7.10	57.70	4.02	30.72	−8.70
Dimethylamine	−7.80	65.20	3.92	48.31	−14.09
Trimethylamine	−10.90	—	3.93	65.85	−19.48
Dimethyl ether	−46.00	63.70	6.42	39.64	−11.45
Formamide	−49.50	—	6.51	25.18	−7.47

(b) *Corrections for the Primary Substitution of Hydrogen by*— CH_3 *Groups*

Basic group	$\Delta(\Delta H_{298}^{\circ})$, kcal/mol	ΔS_{298}°, cal/mol·K	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$
Methane	−2.50	10.35	−2.00	23.20	−9.12
Cyclopentane					
first substitution	−7.04	11.24	1.87	17.55	−6.68
second substitution:					
1,1	−7.55	4.63	−0.67	24.29	−10.21
1,2 (*cis*)	−5.46	6.27	−0.01	22.69	−9.46
1,2 (*trans*)	−7.17	6.43	0.28	21.97	−9.18
1,3 (*cis*)	−6.43	6.43	0.28	21.97	−9.18
1,3 (*trans*)	−6.97	6.43	0.28	21.97	−9.18
additional correction for each following substitution	7.00	—	—	—	—
Cyclohexane					
correction for growth of ring for each added carbon atom	−10.97	1.28	−2.51	30.37	−11.79
first substitution in ring	−7.56	10.78	2.13	18.66	−5.71
second substitution in ring:					
1,1	−6.27	5.18	−2.14	25.69	−10.09
1,2 (*cis*)	−4.16	7.45	−0.65	22.19	−8.84
1,2 (*trans*)	−6.03	6.59	−0.06	22.59	−2.56
1,3 (*cis*)	−7.18	6.48	−0.34	21.49	−7.95
1,3 (*trans*)	−5.21	7.86	0.29	19.29	−7.23
1,4 (*cis*)	−5.23	6.48	0.29	19.29	−7.23
1,4 (*trans*)	−7.13	5.13	−0.72	23.79	−9.91
additional correction for each following substitution	−7.00	—	—	—	—
Benzene					
first substitution	−7.87	12.08	0.78	16.68	−5.41
second substitution:					
1,2	−7.41	7.89	4.27	9.72	−1.87
1,3	−7.83	9.07	0.77	17.46	−6.19
1,4	−7.66	7.81	1.76	13.45	−3.41
third substitution:					
1,2,3	−6.83	9.19	1.41	12.78	−2.71
1,2,4	−7.87	10.42	1.61	12.72	−2.77
1,3,5	−7.96	6.66	2.41	11.30	−1.90

Basic group	$\Delta(\Delta H^{\circ}_{298})$, kcal/mol	ΔS°_{298}, cal/mol·K	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$
Naphthalene					
first substitution	−4.50	12.00	0.36	17.65	−5.88
second substitution:					
1,2	−6.30	8.10	5.20	6.02	−1.18
1,3	−6.50	9.20	1.72	14.18	−3.76
1,4	−8.00	7.80	1.28	14.57	−3.98
Methylamine	−5.70	—	−0.10	17.52	−5.35
Dimethylamino	−6.30	—	−0.10	17.52	−5.35
Trimethylamine	−4.10	—	−0.10	17.52	−5.35
Formamide					
substitution to C atom	−9.00	—	6.11	−1.75	4.75

(c) *Corrections for Secondary Substitutions of Hydrogen by* −CH$_3$ *Groups*

Type Nos. for atoms of type		$\Delta(\Delta H^{\circ}_{298})$, kcal/mol	ΔS°_{298}, cal/mol·K	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$
A	B					
1	1	−4.75	10.10	0.49	22.04	−8.96
1	2	−4.92	9.18	1.09	17.79	−6.47
1	3	−4.42	9.72	1.00	19.88	−8.03
1	4	−5.0	11.00	1.39	17.12	−5.88
1	5	−4.68	10.76	1.09	18.71	−7.16
2	1	−6.31	5.57	−0.30	21.74	−8.77
2	2	−6.33	7.15	−0.64	23.38	−9.97
2	3	−5.25	6.53	0.80	19.27	−7.70
2	4	−3.83	7.46	2.52	16.11	−5.88
2	5	−6.18	6.72	0.37	19.25	−7.72
3	1	−8.22	2.81	−0.28	24.21	−10.49
3	2	−7.00	3.87	−0.93	24.73	−8.95
3	3	−5.19	3.99	−3.27	30.96	−14.06
3	4	−4.94	1.88	−0.14	27.57	−10.27
3	5	−9.20	1.30	0.42	16.20	−4.68
In ethers or esters (1−O−)		−7.00	14.00	−0.01	17.58	−5.33
Substitution of H in acid by −CH$_3$ group with formation of ester		9.50	16.70	0.44	16.63	−4.95

(d) *Corrections for Substitution of Single Bonds by Double and Triple Bonds*

Kind of bond	$\Delta(\Delta H^{\circ}_{298})$, kcal/mol	ΔS°_{298}, cal/mol·K	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$
$1 = 1$	32.88	—2.40	0.21	—8.28	1.36
$1 = 2$	30.00	—0.21	1.12	—11.40	3.32
$1 = 3$	28.23	—0.11	2.18	—15.62	6.42
$2 = 2$ (*cis*)	28.39	—1.19	—3.57	0.14	1.08
$2 = 2$ (*trans*)	27.40	—2.16	1.27	—12.77	3.88
$2 = 3$	26.72	—0.28	—2.02	—10.42	3.83
$3 = 3$	25.70	—0.66	—0.41	—15.14	6.39
$1 \equiv 1$	74.58	—9.85	4.72	—24.36	6.29
$2 \equiv 2$	65.50	—3.97	1.00	—25.70	—9.50
$1 \equiv 2$	69.52	—4.19	3.16	—26.37	8.82

(e) *Additional Corrections for Final Structure of Hydrocarbons*

Correction	$\Delta(\Delta H^{\circ}_{298})$, kcal/mol	ΔS°_{298}, cal/mol·K	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$
Additional correction for each long side chain in ring:					
over 2C in side chain of cyclopentane	—0.45	0.12	—0.48	1.50	1.15
over 2C in side chain of cyclohexane	0.32	—0.39	0.76	2.10	1.30
over 4C in side chain of benzene	—0.70	—0.62	0.22	—0.20	0.08
Additional correction for introduced double bond:					
for conjugated double bonds	13.16	—3.74	2.24	1.16	—0.25
for alternate double bonds	—4.28	—5.12	—0.94	3.88	—3.49
for double bond adjoining aromatic ring					
in side chain less than 5C long	—2.00	—2.65	1.01	—3.24	1.31
in side chain over 4C long	—1.16	—2.65	1.01	—3.24	1.31

(f) *Corrections for Groups Substituting* —CH_3 *Group*

Group	$\Delta(\Delta H^{\circ}_{298})$, kcal/mol	ΔS°_{298}, cal/mol·K	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$
—OH (aliphatic, *meta*, *para*)	−32.70	2.60	3.17	−14.86	5.59
—OH (*ortho*)	−47.70	—	—	—	—
—NO_2	1.20	2.00	6.30	−19.53	10.63
—CN	39.00	4.00	3.64	−13.92	4.53
—Cl; for first Cl at carbon atom	0	0	2.19	−18.85	6.26
—Cl; for each following	4.50	—*	—	—	—
—Br	10.00	3.00*	2.81	−19.41	6.33
—F	−35.00	−1.00*	2.24	−23.61	11.79
—I	24.80	5.00*	2.73	−17.37	4.09
=O (aldehyde)	−12.90	−12.30	3.61	−55.72	22.72
—COOH	−87.00	15.40	8.50	−15.07	7.94
=O (ketone)	−13.20	−2.40	5.02	−66.08	30.21
—SH	15.80	5.20	4.07	−24.96	12.37
—C_6H_5	32.30	21.70	−0.79	53.63	−19.21
—NH_2	12.30	−4.80	1.26	−7.32	2.23

* The calculated corrections for the entropy of the halogens for methyl derivatives should be increased by one. For example, the entropy of methyl chloride is 44.4 (basic group) +10.4 (primary substitution of hydrogen by the —CH_3 group) + 0 (substitution by chlorine) + 1.

8. *Products of Principal Moments of Inertia of Halomethanes and Their Symmetry Numbers Needed for Calculating Thermodynamic Properties According to Yu. Maslov and P. Maslov* [49]
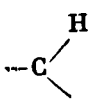
Molecule	$D \times 10^{117}$, g³·cm⁶	σ	Molecule	$D \times 10^{117}$, g³·cm⁶	σ
CF_4	3.24×10^3	12	CH_2I_2	5.69×10^4	2
CCl_4	1.14×10^5	12	CF_2Cl_2	2.50×10^4	2
CBr_4	2.35×10^6	12	CF_2Br_2	1.60×10^5	2
CH_3F	5.92	3	CH_2FCl	4.72×10^2	1
CH_3Cl	17.9	3	CH_2FBr	1.06×10^3	1
CH_3Br	44.6	3	CH_2ClBr	4.54×10^3	1
CH_3I	55.1	3	CH_2ClI	8.82×10^3	1
CHF_3	9.73×10^2	3	CH_2BrI	3.11×10^4	1
CF_3Cl	1.03×10^4	3	CF_2HCl	3.44×10^3	1
CF_3Br	2.38×10^4	3	CF_2HBr	8.22×10^3	1
CF_3I	4.50×10^4	3	CF_2ClBr	6.08×10^4	1
$CHCl_3$	3.30×10^4	3	CCl_2HF	1.09×10^4	1
CCl_3F	6.22×10^4	3	CCl_2HBr	7.50×10^4	1
CCl_3Br	2.56×10^5	3	CCl_2FBr	1.30×10^5	1
$CHBr_3$	6.10×10^5	3	CBr_2HF	8.00×10^4	1
$CFBr_3$	8.30×10^5	3	CBr_2HCl	2.11×10^5	1
$CClBr_3$	1.24×10^6	3	CBr_2FCl	3.22×10^5	1
CH_2F_2	1.17×10^2	2	$CHFClBr$	2.68×10^4	1
CH_2Cl_2	11.87×10^3	2	CHI_3	4.64×10^6	3
CH_2Br_2	1.41×10^4	2	CI_4	16.10×10^6	12

9. *Group Contributions* ΔH°_{form} *and* ΔG°_{form} *According to Franklin, kcal/mol*

Group	0 K		298 K		400 K		500 K	
	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}
—CH$_3$	−8.26	−8.26	−10.12	−4.14	−10.71	−2.00	−11.22	0.24
＞CH$_2$	−3.673	−3.673	−4.926	2.048	−5.223	4.479	−5.46	6.93
—CH	0.18	0.18	−1.09	7.46	−1.17	10.39	−1.12	13.26
—C—	1.74	1.74	0.80	11.44	1.07	15.00	1.45	18.45
H$_2$C =	7.26	7.26	6.25	7.94	5.88	8.57	5.57	9.97
＞C=CH$_2$ (H)	16.73	16.73	15.00	19.13	14.47	20.61	14.01	22.21
＞C=C＜ (*trans*)	19.03	19.03	17.83	23.19	17.57	25.03	17.37	26.93
＞C=C＜ (*cis*)	20.31	20.32	18.88	23.92	18.42	25.68	18.07	27.56
＞C=CH$_2$	18.20	18.20	16.89	22.45	16.68	24.36	16.53	26.31
＞C=C＜ (H)	21.10	21.10	20.19	26.69	20.10	28.88	20.08	31.10
＞C=C＜	25.08	25.08	24.57	32.26	24.74	34.80	24.88	37.36
=C=	33.0	33.0	33.42	32.09	33.59	31.61	33.71	31.08
HC ≡	27.16	27.16	27.10	24.8	27.07	24.01	27.02	23.26
—C ≡	27.12	27.12	27.34	25.65	27.42	26.28	27.48	24.72
＞CH*	4.00	4.00	3.30	4.84	3.09	5.50	2.92	6.13

[*52*, *46*]

600 K		800 K		1000 K		1200 K		1500 K	
ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}
−11.4	2.57	−12.27	7.40	−12.64	12.38	−12.82	17.40	−12.87	24.9
−5.65	9.43	−5.87	14.48	−5.94	19.58	−5.89	24.67	−5.69	32.3
−1.05	16.15	−0.80	21.86	−0.50	27.45	−0.12	33.02	0.33	40.9
1.89	21.82	2.77	28.36	3.60	34.60	4.38	40.71	5.34	49.7
5.30	10.04	4.88	11.69	4.60	13.44	4.44	15.22	4.31	17.9
13.62	23.89	13.03	27.41	12.67	31.05	12.50	34.75	12.39	40.3
17.17	28.86	16.92	32.80	16.82	36.79	16.83	40.79	16.92	46.8
17.77	29.49	17.37	33.48	17.14	37.52	17.09	41.60	17.12	47.8
16.40	28.28	16.23	32.28	16.16	36.28	16.24	40.30	16.39	46.4
20.07	33.32	20.13	37.74	20.13	37.74	20.24	46.46	20.75	52.9
25.06	39.86	25.38	44.78	25.76	49.52	26.2	54.2	26.9	61.2
33.82	30.56	33.95	29.44	34.03	34.03	28.25	27.16	34.06	25.4
26.97	22.50	26.81	21.04	26.65	19.61	26.50	18.22	26.27	16.2
27.50	24.19	27.53	23.07	27.49	21.96	27.51	20.84	27.46	19.2
2.79	6.78	2.59	8.15	2.47	9.56	2.42	10.97	2.46	13.1

Group	0 K		298 K		400 K		500 K	
	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}
$>$C—	5.76	5.76	5.57	8.76	5.59	9.34	5.63	10.23
$>$C—**	5.29	5.29	4.28	5.43	4.33	5.80	4.28	6.49
—CH$_2$	11.3	11.3	10.08	13.17	9.81	14.17	9.64	15.26
—C$<^H$	12.65	12.65	12.04	16.36	12.11	17.70	12.16	19.15
Cycloparaffin ring:								
C$_6$	1.10	1.10	—0.45	—6.35	—1.13	—7.98	—1.67	—9.61
C$_5$	6.72	6.72	5.68	—2.66	4.94	—5.58	4.28	—8.06
C$_4$	18.8	18.8	18.4	8.0	18.0	4.0	17.6	0
C$_3$	24.4	24.4	24.22	14.51	23.87	11.33	23.58	8.12
Correction factors for paraffin chains:								
ethyl side chain	1.5	1.5	0.8	—	0.8	—	0.8	—
three adjacent CH-groups	1.6	1.6	2.3	—	2.3	—	2.3	—
adjacent quaternary carbon atoms	5.0	5.0	5.4	5.8	5.4	5.9	5.4	6.1
Adjacent C- and CH-groups	2.5	2.5	2.5		2.5		2.5	
Quaternary C not adjacent to terminal methyl	2.1	2.1	1.7	1	1.7		1.7	

600 K		800 K		1000 K		1200 K		1500 K	
ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}
5.62	11.18	5.72	13.08	5.85	14.76	5.99	16.59	6.14	19.2
4.27	7.28	4.56	8.05	4.16	9.18	3.51	10.95	—	12.3
9.48	16.41	9.25	18.75	9.12	21.16	23.56	23.56	9.05	27.2
12.17	20.55	12.27	23.29	12.43	23.06	12.59	28.74	12.66	32.7
−1.96	−11.58	−2.12	−14.50	−1.86	−17.85	−1.41	−20.60	−0.52	−26.0
3.74	−10.52	3.00	−15.25	2.57	−19.59	2.22	−24.02	−1.96	−30.5
17.0	−4.0	16.4	−6.0	15.6	−12.8	15.2	−16.4	14.4	−25.2
23.38	5.06	22.89	−0.91	22.50	6.82	22.15	−12.60	21.60	−21.4
0.8	0.7	0.8	—	0.8	—	0.8	—	0.8	—
2.3	2.1	2.3	—	2.3	—	2.3	—	2.3	—
5.4	6.3	5.4	6.5	5.4	7.0	5.4	—	5.4	—
2.5	3.6	2.5		2.5		2.5		2.5	
1.7	1.0	1.7		1.7		1.7		1.7	

Group	0 K		298 K		400 K		500 K	
	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}
Correction factors for substitutions in aromatic nuclei:								
1,2-dimethyl or 1,3-methylethyl	0.1		0.6		0.6		0.6	
1,2-methylethyl or 1,2,3-trimethyl	0.9		1.4		1.4			
1,2-substitution								
1,3-substitution		0.9						
1,2,3-substitution								
Correction for symmetry		0						
—OH (primary)	−40.1	−40.1	−41.9	−36.6				
—OH (secondary)	−43.1	−43.1	−44.9	−42.1				
—OH (tertiary)	−46.9	−46.9	−49.2	−44.7				
—OH (phenol)	−44.0	−44.0	−46.9	−39.9				
H—C=O	−32.7	−32.7	−33.9	−27.9				
C=O	−30.6	−30.6	−31.6	−28.0				
—C(=O)OH	−93.1	−93.1	−94.6	−87.1				

600 K		800 K		1000 K		1200 K		1500 K	
ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}
0.6	0.5	0.6		0.6		0.6		0.6	
1.4	−0.7	0.6		0.6		0.6		0.6	
	0.5								
	−0.7								
	1.0								
	RT								
−42.2	−31.1			−40.6	−24.0				
−44.4	−37.4			−41.4	−33.6				
−48.9	−37.1			−44.4	−31.4				
−45.6	−31.1			−39.9	−23.2				
−34.0	−21.7			−33.9	−13.5				
−31.2	−25.9			−30.5	−22.6				
−93.0	−79.6			−90.4	−70.9				

Group	0 K		293 K		400 K		500 K	
	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}
$-C\big(\!\!\overset{O}{\underset{O-}{}}\!\!\big)$ (ester)			−79.8	−71.6				
$-O-$ (ether)			−27.2	−23.8				
$-C\big(\!\!\overset{O}{\underset{O}{}}\!\!\big)\ -C\big(\!\!\overset{}{\underset{O}{}}\!\!\big)$			−102.6	−93.9				
$--NH_2$			2.8	−6.4				
$>NH$			12.0					
$>N-$			−19.2					
$-NH_2$			−0.8					
$-NO_2$			−8.5					
$-ONO$			−10.9					
$-ONO_2$			−18.4					
$-C\equiv N$			29.5					
$-N=C<$			44.4					
$-SH$			5.7	3.1				
$-S-$			11.6	10.6				
$--S--$			11.3	7.8				
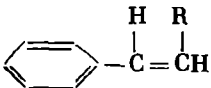
* Indicates a resonance structure, for example the $>CH$ groups in benzene.
** Estimated with the aid of extrapolation and interpolation.

600 K		800 K		1000 K		1200 K		1500 K	
ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}	ΔH°_{form}	ΔG°_{form}

10. Group Contributions for Calculating $(\Delta H^\circ_T)_{form}$ *According to Souders, Matthews, and Hurd* [55]

(a) *Contributions for Calculating* $(\Delta H^\circ_{298})_{form}$

Group	Primary contributions, kcal/mol			
	Aliphatic hydrocarbon	Six-member naphthenic ring	Five-member naphthenic ring	Aromatic ring
—CH₃	—10.05			
—CH₂—	—4.95	—4.91	—3.68	
—ĊH (2d carbon)*	—1.57	—1.53	—1.63	
(3d or higher)*	—0.88			
—Ċ— (2d carbon)*	0.85	0.85	0.85	
(3d or higher)*	2.45			
H₂C=	5.80			
HĊ=**	9.28	9.20	9.57	3.33
HĊ= (*trans*)	8.70			
—Ċ=	10.84	10.75	11.10	5.48
=C=	34.09			
HC ≡	27.04			
—C ≡	27.65			

Group	Conjugation and adjacency contributions***
H H | | =C—C= (aliphatics)	—3.28
H | | =C—C= (aliphatics)	—4.45
| | =C—C= (aliphatics)	—2.10

Appendix 10(a) (concluded)

Group	Conjugation and adjacency contributions***
H H | | =C—C= (five-member naphthenic ring)	−2.88
H H | | =C—C= (six-member naphthenic ring)	−1.76
⬡ H R —C=CH	−2.01
Each pair *ortho* groups in aromatics	0.69
Ethyl side chain (aliphatics)	0.88
| | —C—C— | | H H	0.75
| | —C—C— | H	2.39
| | | —C—C—C— | | | H H H	2.30
| | —C—C— | |	4.61
—C=C— | |	2.61

* Indicates position of group in the longest chain of an aliphatic hydrocarbon measured from the shortest end.
** To be used when groups are in the adjacent (*cis*) position or when there is no *cis-trans* effect.
*** To be added to the primary group contributions whenever these molecular groups appear. The symbol — indicates a C—C bond, and R indicates either H or C.

(b) *Vibrational Group Contributions (kcal/mol)*

Group	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	2000
Paraffins:														
—CH₃	−0.016	−1.099	−2.101	−3.839	−4.594	−5.278	−5.278	−5.905	−6.480	−7.010	−7.505	−7.973	−8.419	−10.527
—CH₂—	−0.008	−0.582	−1.066	−1.463	−1.793	−2.060	−2.276	−2.448	−2.580	−2.082	−2.756	−2.821	−2.864	−2.963
—CH—	0.001	0.017	0.043	0.174	0.553	0.572	0.825	1.107	1.412	1.736	2.075	2.425	2.782	4.623
—C—	0.012	0.664	1.377	2.126	2.888	3.657	4.432	5.210	5.991	6.774	7.557	8.339	9.119	12.978
Cycloparaffins:														
—CH₂— in five-member ring	−0.008	−0.627	−1.160	−1.187	−1.985	−2.304	−2.570	−2.791	−2.974	−3.723	−3.245	−3.348	−3.435	−3.735
—CH₃— in six-member ring	−0.008	−0.570	−1.036	−1.412	−1.719	−1.965	−2.156	−2.303	−2.413	−2.491	−2.544	−2.580	−2.603	−2.622
Aromatic hydro-carbons:														
HC=	−0.004	−0.343	−0.643	−0.905	−1.146	−1.364	−1.561	−1.740	−1.904	−2.054	−2.194	−2.325	−2.451	−3.054
—C=	0.007	0.287	0.577	0.873	1.169	1.463	1.758	2.052	2.345	2.637	2.926	3.212	33.494	4.870
Acetylene hy-drocarbons:														
HC≡	−0.004	−0.379	−0.764	−1.154	−1.563	−1.980	−2.399	−2.819	−3.234	−3.646	−4.054	−4.460	−4.866	−6.905
—C≡	0.004	0.129	0.227	0.300	0.346	0.373	0.387	0.392	0.390	0.384	0.976	0.364	0.347	0.207
Olefins:														
H₂C=	−0.011	−0.767	−1.478	−2.139	−2.782	−3.348	−3.898	−4.419	−4.911	−5.380	−5.830	−6.265	−6.689	−8.725
HC=	−0.003	−0.245	−0.447	−0.608	−0.742	−0.853	0.944	−1.014	−1.067	−1.105	−1.132	−1.152	−1.167	−1.221
—C=	0.007	0.363	0.727	1.098	1.468	1.835	2.202	2.569	2.939	3.311	3.685	4.058	4.428	6.236
=C=	0.003	0.156	0.285	0.389	0.465	0.517	0.557	0.587	0.610	0.629	0.643	0.652	0.655	0.607

Temperature, K

(c) *Internal-Rotational Contributions (kcal/mol)*

T, K	$-CH_2-CH_2-$	CH_3-CH_2-	$-R-CH$	$-C-$	$R-CH=(cis)$	$R-CH=(trans)$	$=CH-CH=$	$\equiv C-C\equiv$	$-C\equiv$	$R(T-298.15)$
300	0.005	0.004	0.003	0.004	0.003	0.002	0.005	0.001	0.003	0.015
400	0.304	0.218	0.221	0.214	0.196	0.123	0.325	0.086	0.218	0.809
500	0.560	0.432	0.437	0.435	0.370	0.235	0.637	0.154	0.421	1.604
600	0.785	0.634	0.642	0.655	0.527	0.343	0.918	0.207	0.608	2.398
700	0.986	0.822	0.834	0.868	0.673	0.449	1.173	0.250	0.779	3.193
800	1.168	0.997	1.013	1.070	0.809	0.554	1.408	0.286	0.938	3.988
900	1.335	1.161	1.181	1.261	0.938	0.656	1.625	0.321	1.089	4.782
1000	1.438	1.319	1.339	1.441	1.061	0.760	1.828	0.353	1.230	5.577
1100	1.636	1.465	1.488	1.613	1.181	0.862	2.019	0.382	1.366	6.371
1200	1.775	1.606	1.631	1.776	1.297	0.963	2.201	0.409	1.496	7.166
1300	1.908	1.742	1.769	1.932	1.410	1.064	2.375	0.434	1.623	7.961
1400	2.036	1.873	1.902	2.082	1.522	1.165	2.542	0.458	1.746	8.755
1500	2.159	2.001	2.032	2.227	1.632	1.266	2.702	0.480	1.865	9.550
2000	2.736	2.599	2.638	2.894	2.171	1.769	3.424	0.579	2.435	13.523

11. *Characteristic Temperatures of Selected Gases* [18]

Gas	θ	Gas	θ_1	θ_2	θ_3	θ_4	θ_5
Br_2	461	CCl_4	342 (2)	440 (3)	630	1114 (3)	
CO	3085	CH_4	1870 (3)	2170 (2)	4320 (3)	4400	
Cl_2	801	COS	746 (3)	1230	2936		
F_2	1533	CO_2	960 (2)	1830	3380		
HBr	4200	CS_2	568 (2)	939	2194		
HCl	4130	C_2H_2	859 (2)	1044 (2)	2838	4693 (3)	4826
HF	5790	C_2N_2	730 (2)	1060 (2)	1230 (2)	3080	3340
HI	3245	HCN	1020 (2)	2290	4710		
H_2	6130	H_2O	2290	5730	5510		
I_2	305	H_2S	1810	3750 (2)			
NO	2705	NH_3	1357	2336 (2)	4176	4776 (2)	
N_2	3350	N_2O	844 (2)	1842	3195		
O_2	2224	SO_2	750	1650	1950		

Note. The figures in parentheses are the number of degeneracies.

12. Einstein's Functions for Calculating the Vibrational Component of the Heat Capacity of a Gas, cal/mol·K [18]

$\frac{\Theta}{T}$	c_{vib}	$\frac{\Theta}{T}$	c_{vib}	$\frac{\Theta}{T}$	c_{vib}	$\frac{\Theta}{T}$	c_{vib}
0	1.986	1.10	1.798	2.30	1.302	4.80	0.383
0.10	1.983	1.15	1.782	2.40	1.256	5.00	0.339
0.15	1.981	1.20	1.765	2.50	1.210	5.20	0.300
0.20	1.979	1.25	1.747	2.60	1.164	5.40	0.262
0.25	1.976	1.30	1.729	2.70	1.119	5.60	0.232
0.30	1.974	1.35	1.711	2.80	1.074	5.80	0.204
0.35	1.967	1.40	1.692	2.90	1.030	6.00	0.178
0.40	1.960	1.45	1.673	3.00	0.986	6.40	0.136
0.45	1.952	1.50	1.659	3.10	0.943	6.80	0.103
0.50	1.945	1.55	1.633	3.20	0.901	7.20	0.077
0.55	1.938	1.60	1.612	3.30	0.860	7.60	0.057
0.60	1.928	1.65	1.592	3.40	0.820	8.00	0.0427
0.65	1.918	1.70	1.570	3.50	0.781	8.40	0.032
0.70	1.908	1.75	1.549	3.60	0.744	8.80	0.023
0.75	1.884	1.80	1.527	3.70	0.707	9.20	0.017
0.80	1.884	1.85	1.505	3.80	0.672	9.60	0.012
0.85	1.871	1.90	1.483	3.90	0.637	10.00	0.009
0.90	1.858	1.95	1.461	4.00	0.604	11.00	0.004
0.95	1.844	2.00	1.439	4.20	0.542	12.00	0.0017
1.00	1.829	2.10	1.393	4.40	0.484	13.00	0.0007
1.05	1.814	2.20	1.348	4.60	0.431		

13. Heat Capacity C_p° of Standard Substances of Aliphatic and Cyclic Compounds According to Kelley, Parks, and Huffman, cal/mol·K [57, 25]

T, K	Aliphatic compounds	Cyclic compounds	T, K	Aliphatic compounds	Cyclic compounds
20	1.38	2.65	100	10.30	15.15
30	2.87	5.45	105	10.65	15.61
40	4.40	7.80	110	11.00	16.05
50	5.75	9.65	115	11.34	16.50
60	6.92	11.00	120	11.70	16.90
70	7.95	12.15			
80	8.84	13.22			
90	9.64	14.20			
95	9.98	14.67	$\int_0^{90} C_p^\circ \, dT$	432	697
			S_{90}°	8.05	13.7

14. Constants of Eq. (2.34) for Calculating Standard Entropies at 298.15 K for Selected Kinds of Solid Inorganic Substances [59, 8]

Kind of compound	A		B	
	J/mol·K	cal/mol·K	J/mol·K	cal/mol·K
Me_2O	87.45	20.9	—87.45	—20.9
MeO	60.67	14.5	—70.71	—16.9
Me_2O_3	138.49	33.1	—227.61	—54.4
MeO_2	64.02	15.3	—68.62	—16.4
Me_2O_5	133.05	31.8	—209.20	—50.0
MeHal	62.76	15.0	—38.07	—9.1
$MeHal_2$	136.82	32.7	—185.35	—44.3
$MeHalO_3$	35.98	8.6	68.20	16.3
MeS	69.87	16.7	—73.22	—17.5
$MeNO_3$	90.79	21.7	—60.67	—14.5

15. Constants A and B of Eqs. (2.35) and (2.36) for Calculating Standard Entropies at 298.15 K for Selected Gases [59, 5]

Gas	A	B		log B	
		J/mol·K	cal/mol·K	J/mol·K	cal/mol·K
Diatomic	0.136	124.68	29.8	2.096	1.474
Triatomic	0.211	101.67	24.3	2.007	1.386
Tetratomic	0.221	101.25	24.2	2.005	1.384
Pentatomic	0.213	102.51	24.5	2.011	1.389
Sexatomic	0.294	82.42	19.7	1.916	1.294

16. Values of M_n for Calculating Thermodynamic Functions According to Temkin and Shwartsman [67]

$$M_0 = \frac{T}{298.15} + \frac{298.15}{T} - 1$$

$$M_n = \frac{T^n}{n(n+1)} + \frac{298.15^{n+1}}{(n+1)T} - \frac{298.15^n}{n} \quad \text{(at } n \neq 0\text{)}$$

T, K	M_0	$M_1 \times 10^{-3}$	$M_2 \times 10^{-6}$	$M_{-2} \times 10^5$
300	0.0000	0.0000	0.0000	0.0000
400	0.0392	0.0130	0.0043	0.0364
500	0.1133	0.0407	0.0149	0.0916
600	0.1962	0.0759	0.0303	0.1423
700	0.2794	0.1153	0.0498	0.1853
800	0.3597	0.1574	0.0733	0.2213
900	0.4361	0.2012	0.1004	0.2521
1000	0.5088	0.2463	0.1134	0.2783
1100	0.5765	0.2922	0.1652	0.2988
1200	0.6410	0.3389	0.2029	0.3176
1300	0.7019	0.3860	0.2440	0.3340
1400	0.7595	0.4336	0.2886	0.34835
1500	0.8141	0.4814	0.3362	0.3610
1600	0.8665	0.5296	0.3877	0.3723
1700	0.9162	0.5780	0.4424	0.3824
1800	0.9635	0.6265	0.5005	0.3915
1900	1.009	0.6752	0.5619	0.3998
2000	1.0525	0.7240	0.6265	0.4072

17. Group Contributions and Corrections for Deviation in Structure of Hydrocarbon for Calculating $(\Delta G_T^\circ)_{\text{form}}$ According to Chermin and van Krevelen [62, 63]

(a) *Coefficients of Group Contributions of Equation $(\Delta G_T^\circ)_{\text{form}} = A + BT$, kcal/mol, for Alkanes, Naphthenes, Alkenes, Alkynes, and Aromatic Hydrocarbons*

Group	300–600 K		600–1500 K	
	A	$B \times 10^2$	A	$B \times 10^2$
CH$_4$	−18.719	2.180	−21.161	2.587
—CH$_3$	−10.833	2.176	−12.393	2.436
$>$CH$_2$	−5.283	2.443	−5.913	2.548

Group	300-600 K		600-1500 K	
	A	$B\times10^2$	A	$B\times10^2$
$>$CH	-0.756	2.942	-0.756	2.942
$>$C$<$	3.060	3.636	3.840	3.506
$H_2C=CH_2$	11.653	1.552	9.451	1.889
$H_2C=C<^H$	14.281	1.642	13.513	1.770
$H_2C=C<$	16.823	1.864	15.785	2.037
$^H>C=C<^H$ *(cis)*	18.407	1.834	16.781	2.114
$^H>C=C<^H$ *(trans)*	17.019	2.007	16.755	2.051
$^H>C=C<$	20.273	2.306	19.913	2.366
$>C=C<$	23.955	2.839	25.731	2.543
$H_2C=C=CH_2$	45.293	1.010	43.439	1.319
$H_2C=C=C<^H$	48.871	1.063	48.133	1.186
$H_2C=C=C<$	51.159	1.481	51.159	1.481
$^H>C=C=C<$	53.176	1.528	52.690	1.609
$HC\equiv$	27.104	-0.775	26.678	-0.704
$-C\equiv$	27.478	-0.617	27.346	-0.595
$HC<$ (aromatics)	3.100	0.610	2.536	0.704
$-C<$ (aromatics)	5.280	0.994	5.634	0.935
$\leftarrow C<$ (aromatics)	2.260	0.553	2.566	0.502

Group	300-600 K		600-1500 K	
	A	$B \times 10^2$	A	$B \times 10^2$
Conjugated alkenes:				
$H_2C \leftrightarrow$	9.634	1.088	8.980	1.197
HC⟨	3.100	0.610	2.536	0.704
HC⟨	12.302	1.438	12.408	1.420
←C⟨	5.280	0.994	5.634	0.935

(b) Coefficients of Corrections for Deviation in Structure of Alkanes, Naphthenes, and Aromatic Hydrocarbons

Correction	300-600 K		600-1500 K	
	A	$B \times 10^2$	A	$B \times 10^2$
Branching in alkanes:				
side chain with 2 or more C atoms	1.31	0.0	1.31	0.0
three adjacent HC⟨ groups	2.312	0.0	2.312	0.0
adjacent HC⟨ and ⟩C⟨ groups	1.625	0.0	1.625	0.0
two adjacent ⟩C⟨ groups	2.543	0.0	2.543	0.0
Formation of naphthene rings:				
three-member	27.215	—3.147	26.495	—3.027
four-member	25.689	—2.901	24.459	—2.696
five-member	5.511	—2.583	3.417	—2.234
six-member	—0.707	—1.623	—1.145	—1.550
cyclopentene	3.455	—2.448	2.189	—2.237
cyclohexene	—1.043	—2.070	—0.737	—2.121
Branching in naphthenes:				
five-member ring:				
single branching	—0.665	—0.065	—0.443	—0.102
double branching:				
1,1 position	—1.880	—0.138	—1.112	—0.266
cis 1,2 position	—1.485	0.245	—0.939	—0.159
trans 1,2 position	—2.163	—0.138	—1.377	—0.269
cis 1,3 position	—1.423	0.0	—0.637	—0.131
trans 1,3 position	—1.888	0.138	—1.048	—0.278

Appendix 17(b) (concluded)

Correction	300-600 K		600-1500 K	
	A	*B*×10²	*A*	*B*×10³
six-member ring:				
single branching	—0.370	—0.106	0.452	—0.243
double branching:				
1,1 position	—1.722	0.0	—0.432	—0.215
cis 1,2 position	—0.500	0.0	1.432	—0.322
trans 1,2 position	—2.003	—0.138	—0.173	—0.443
cis 1,3 position	—3.055	0.0	—1.687	—0.228
trans 1,3 position	—1.718	0.0	0.262	—0.330
cis 1,4 position	—1.152	0.0	0.0	—0.192
trans 1,4 position	—3.125	0.034	—1.205	—0.286
Branching in aromatic rings:				
1,2 position	0.955	0.055	1.687	—0.067
1,3 position	0.352	—0.057	0.574	—0.094
1,4 position	—0.183	0.105	0.615	—0.028
1,2,3 position	1.453	—0.112	1.039	—0.043
1,2,4 position	0.297	—0.070	0.243	—0.061
1,3,5 position	—0.320	—0.137	—0.436	—0.116
1,2,3,4 position	3.664	—0.007	4.456	—0.139
1,2,3,5 position	2.861	0.025	3.359	—0.058
1,2,4,5 position	2.736	—0.150	3.072	—0.206
five substitutions	4.400	0.091	5.468	—0.087
six substitutions	8.254	0.260	10.006	—0.032

(c) Coefficients of Group Contributions for Non-Hydrocarbon Groups

Group	300-600 K		600-1500 K	
	A	*B*×10³	*A*	*B*×10³
H_2O	—58.076	1.154	—59.138	1.316
—O—	—15.790	—0.85	—	—
O⟨	—18.37	0.80	—16.07	0.40
H_2CO	—29.118	0.653	—30.327	0.854
HC=O	—29.16	0.663	—30.102	0.802
⟩C=O	—28.08	0.91	—28.08	0.91

Group	300-600 K		600-1500 K	
	A	$B \times 10^2$	A	$B \times 10^3$
HC=O | OH	—87.66	2.473	—90.569	2.958
—C=O | OH	—98.39	2.86	—98.83	2.93
—C=O | O—	—92.62	2.61	—92.62	2.61
H_2C=CO	—14.515	0.295	—14.515	0.295
HC=C=O	—12.86	0.46	—12.86	0.46
C=C=O	—9.62	0.72	—9.38	0.73
HCN	31.179	—0.826	30.874	—0.775
—C≡N	30.75	—0.72	30.75	—0.72
—N=C	46.32	—0.89	46.32	—0.89
NH_3	—11.606	2.556	—12.972	2.784
—NH_2	2.82	2.71	—6.78	3.98
NH	12.93	3.16	12.93	3.16
N—	19.46	3.82	19.46	3.82
N	11.32	1.11	12.26	0.96
—NO_2	—9.0	3.70	—14.19	4.38
HF	—64.476	—0.145	—64.884	—0.081
F—	—45.10	—0.20	—	—
HCl	—22.10	—0.215	—22.460	—0.156
—Cl	—8.25	0.0	—8.25	0.0
HBr	—12.533	—0.234	—13.010	—0.158
—Br	—1.62	—0.26	—1.62	—0.26
HI	—1.130	—2.215	—1.718	—0.176
—I	7.80	0.0	7.80	0.0
H_2S	—20.552	1.026	—21.366	1.167
—S—	—3.32	1.42	—3.32	1.44
S	—0.97	0.51	—0.65	0.44

Group	300-600 K		600-1500 K	
	A	$B \times 10^2$	A	$B \times 10^2$
—S—S—	—18.606	2.664	—18.204	2.597
—SH (primary)	—11.827	0.975	—11.815	0.973
=SO	—30.19	3.39	—30.19	3.39
=SO$_2$	—82.58	5.58	—80.69	5.26
—OH (primary)	—42.959	1.134	—43.103	1.158
—OH (secondary)	—44.538	1.18	—44.232	1.136
—OH (tertiary)	—49.407	1.020	—49.193	1.001
—OH (aryl)	—45.644	1.533	—45.506	1.510
Rings:				
(ring structure C—C with O)	12.86	—0.63	12.86	—0.63
(ring structure C—C, C—C with O)	—5.82	0.25	—3.53	—0.16

18. Solution of the Equation of the Law of Mass Action for Different Types of Reactions [24]

y	Type I: $A \rightleftarrows B$ $K = \dfrac{y}{1-y}$	Type II: $A \rightleftarrows 2B$ $K = \dfrac{4y^2 p}{1-y^2}$	Type III: $A \rightleftarrows 3B$ $K = \dfrac{27y^3 p^2}{(1-y)(1+2y)^2}$
	$\log K = \log M$	$\log K - \log p = \log M$	$\log K - 2 \log p = \log M$
0.01	—1.996	—3.398	—4.581
0.02	—1.690	—2.796	—3.691
0.04	—1.380	—2.193	—2.811
0.05	—1.279	—1.999	—2.532
0.10	—0.954	—1.394	—1.682
0.20	—0.602	—0.778	—0.861
0.30	—0.358	—0.408	—0.391
0.40	—0.174	—0.118	—0.051
0.50	0.000	0.125	0.227
0.60	0.176	0.352	0.479
0.70	0.368	0.585	0.729
0.80	0.602	0.852	1.010
0.90	0.954	1.232	1.400

ν	Type I: $A \rightleftarrows B$ $K = \dfrac{y}{1-y}$	Type II: $A \rightleftarrows 2B$ $K = \dfrac{4y^2p}{1-y^2}$	Type III: $A \rightleftarrows 3B$ $K = \dfrac{27y^3p^2}{(1-y)(1+2y)^2}$
	$\log K = \log M$	$\log K - \log p = \log M$	$\log K - 2 \log p = \log M$
0.95	1.279	1.568	1.741
0.97	1.510	1.804	1.978
0.99	1.996	2.294	2.470
0.995	2.299	2.598	2.774

ν	IV: $2A \rightleftarrows B$ $K = \dfrac{y(2-y)}{4(1-y)^2p}$	V: $2A \rightleftarrows 3B$ $K = \dfrac{27y^3p}{4(1-y)^2(2+y)}$	VI: $A \rightleftarrows B + 0.5C$ $K = \dfrac{0.25y^{1.5}p^{0.5}}{(1-y)(1+0.5y)^{0.5}}$
	$\log K + \log p = \log M$	$\log K - \log p = \log M$	$\log K - 0.5 \log p = \log M$
0.01	−2.297	−5.465	−3.1098
0.02	−1.987	−4.556	−2.6959
0.04	−1.672	−3.639	−2.1975
0.05	−1.568	−3.341	−1.7886
0.10	−1.232	−2.401	−1.6189
0.20	−0.852	−1.416	−1.1264
0.30	−0.585	−0.791	−0.8139
0.40	−0.352	−0.310	−0.5687
0.50	−0.125	0.130	−0.3530
0.60	0.118	0.545	−0.1458
0.70	0.403	0.979	0.0714
0.80	0.778	1.489	0.3166
0.90	1.392	2.230	0.6965
0.95	1.999	2.895	1.1290
0.97	2.443	3.363	1.2634
0.99	3.398	4.341	1.7519
0.995	4.000	4.801	2.0560

ν	VII: $A \rightleftarrows B + C$ $K = \dfrac{y^2p}{1-y^2}$	VIII: $A \rightleftarrows B + 2C$ $K = \dfrac{4y^3p^2}{(1-y)(1+2y)^2}$	IX: $A \rightleftarrows B + 3C$ $K = \dfrac{27y^4p^3}{(1-y)(1+3y)^3}$
	$\log K - \log p = \log M$	$\log K - 2 \log p = \log M$	$\log K - 3 \log p = \log M$
0.01	−3.9996	−5.410	−7.603
0.02	−3.3979	−4.520	−5.432
0.04	−2.7951	−3.641	−4.290
0.05	−2.6010	−3.462	−3.933

ν	VII: $A \rightleftharpoons B + C$ $$K = \frac{y^2 p}{1 - y^2}$$ $\log K - \log p = \log M$	VIII: $A \rightleftharpoons B + 2C$ $$K = \frac{4y^3 p^2}{(1 - y)(1 + 2y)^2}$$ $\log K - 2 \log p = \log M$	IX: $A \rightleftharpoons B + 3C$ $$K = \frac{27 y^4 p^3}{(1 - y)(1 + 3y)^3}$$ $\log K - 3 \log p = \log M$
0.10	—1.9956	—2.510	—2.865
0.20	—1.3822	—1.690	—1.880
0.30	—1.0048	—1.220	—1.341
0.40	—0.7202	—0.879	—0.966
0.50	—0.4771	—0.602	—0.666
0.60	—0.2499	—0.350	—0.400
0.70	—0.0174	—0.100	—0.139
0.80	0.2499	0.180	0.148
0.90	0.6297	0.445	0.496
0.95	0.9664	0.912	0.887
0.97	1.2284	1.149	1.125
0.99	1.6924	1.640	1.618
0.995	1.9978	1.945	1.923

ν	X: $A \rightleftharpoons B + 4C$ $$K = \frac{256 y^5 p^4}{(1 - y)(1 + 4y)^4}$$ $\log K - 4 \log p = \log M$	XI: $A + B \rightleftharpoons C$ $$K = \frac{y(2 - y)}{(1 - y)^2 p}$$ $\log K + \log p = \log M$	XII: $2A + B \rightleftharpoons C$ $$K = \frac{y(3 - 2y)^2}{4(1 - y)^3 p^2}$$ $\log K + 2 \log p = \log M$
0.01	—7.658	—1.692	—1.640
0.02	—6.212	—1.385	—1.332
0.04	—4.751	—1.070	—1.016
0.05	—4.391	—0.967	—0.911
0.10	—3.130	—0.630	—0.570
0.20	—2.010	—0.250	—0.180
0.30	—1.421	0.017	0.100
0.40	—1.020	0.250	0.350
0.50	—0.704	0.477	0.602
0.60	—0.429	0.720	0.880
0.70	—0.162	1.005	1.220
0.80	0.130	1.380	1.690
0.90	0.528	1.996	2.510
0.95	0.973	2.601	3.362
0.97	1.112	3.045	4.568
0.99	1.604	4.000	5.411
0.995	1.909	4.602	6.903

y	XIII: $3A + B \rightleftarrows C$ $K = \dfrac{y(4-3y)^3}{27(1-y)^4 p^3}$ $\log K + 3\log p = \log M$	XIV: $A + 4B \rightleftarrows C$ $K = \dfrac{y(5-4y)^4}{256(1-y)^5 p^4}$ $\log K + 4\log p = \log M$	XV: $3A + B \rightleftarrows 2C$ $K = \dfrac{16y^2(2-y)^2}{27(1-y)^4 p^2}$ $\log K + 2\log p = \log M$
0.01	−1.618	−1.6080	−3.612
0.02	−1.309	−1.2952	−2.997
0.04	−0.992	−0.9784	−2.368
0.05	−0.887	−0.8729	−2.160
0.10	−0.544	−0.5280	−1.487
0.20	−0.148	−0.1299	−0.727
0.30	−0.139	0.1628	−0.192
0.40	0.399	0.4219	0.273
0.50	0.665	0.7042	0.727
0.60	0.966	1.0195	1.213
0.70	1.341	1.4210	1.782
0.80	1.880	2.0111	2.533
0.90	2.865	3.1300	3.764
0.95	3.933	4.3913	4.975
0.97	4.859	5.3900	5.864
0.99	6.603	7.6554	7.773
0.995	6.950	10.1290	8.972

v	XVI: $A + B \rightleftarrows 2C$ $K = \dfrac{4y}{(1-y)^2}$ $\log K = \log M$	XVII: $A + B \rightleftarrows 3C$ $K = \dfrac{27y^3 p}{(1-y)^2(2+y)}$ $\log K - \log p = \log M$	XVIII: $A + B \rightleftarrows C + D$ $K = \dfrac{y^2}{(1-y)^2}$ $\log K = \log M$
0.01	−3.389	−4.863	−3.991
0.02	−2.778	−3.953	−3.380
0.04	−2.158	−3.036	−2.760
0.05	−1.955	−2.739	−2.557
0.10	−1.306	−1.799	−1.908
0.20	−0.602	−0.814	−1.204
0.30	−0.134	−0.189	−0.736
0.40	0.250	0.301	−0.352
0.50	0.602	0.732	0
0.60	0.952	1.147	0.352
0.70	1.338	1.581	0.736
0.80	1.806	2.091	1.204
0.90	2.511	2.832	1.908

ν	XVI: A + B $\rightleftarrows$ 2C $K = \dfrac{4y}{(1-y)^2}$	XVII: A + B $\rightleftarrows$ 3C $K = \dfrac{27y^3 p}{(1-y)^2(2+y)}$	XVIII: A + B $\rightleftarrows$ C + D $K = \dfrac{y^2}{(1-y)^2}$
	$\log K = \log M$	$\log K - \log p = \log M$	$\log M = \log K$
0.95	3.160	3.497	2.557
0.97	3.621	3.965	3.019
0.99	4.593	4.943	3.991
0.995	5.200	5.550	4.598

ν	XIX: A + 1.5 B $\rightleftarrows$ C + D $K = \dfrac{y^2\sqrt{\dfrac{2.5-0.5y}{p}}}{1.5^{1.5}(1-y)^{2.5}}$	XX: 2A + B $\rightleftarrows$ C + D $K = \dfrac{y^2(3-y)}{4(1-y)^3 p}$	XXI: 3A + B $\rightleftarrows$ C + D $K = \dfrac{4y^2(2-y)^2}{27(1-y)^4 p^2}$
	$\log K + 0.5\log p = \log M$	$\log K + \log p = \log M$	$\log K + 2\log p = \log M$
0.01	−4.055	−4.113	−4.214
0.02	−3.342	−3.500	−3.499
0.04	−2.839	−2.874	−2.870
0.05	−2.614	−2.667	−2.763
0.10	−1.955	−2.002	−2.039
0.20	−1.230	−1.262	−1.329
0.30	−0.737	−0.752	−0.794
0.40	−0.325	−0.317	−0.330
0.50	0.062	0.097	0.125
0.60	0.458	0.528	0.611
0.70	0.899	1.018	1.180
0.80	1.451	1.643	1.931
0.90	2.300	2.629	3.162
0.95	3.097	3.568	4.373
0.97	3.973	4.248	5.353
0.99	4.878	5.692	7.271
0.995	5.936	6.598	8.472

y	XXII: $4A + B \rightleftarrows C + D$ $K = \dfrac{y^2 (5 - 3y)^3}{256 (1 - y)^5 p^3}$	XXIII: $2A + B \rightleftarrows 2C + D$ $K = \dfrac{y^3}{(1 - y)^3}$	XXIV: $4A + B \rightleftarrows 2C + D$ $K = \dfrac{y^3 (5 - 2y)^2}{64 (1 - y)^5 p^2}$
	$\log K + 3 \log p = \log M$	$\log K = \log M$	$\log K + 2 \log p = \log M$
0.01	−4.297	−5.987	−6.390
0.02	−3.681	−5.071	−5.468
0.04	−3.066	−4.141	−4.535
0.05	−2.842	−3.836	−4.217
0.10	−2.163	−2.863	−3.215
0.20	−1.391	−1.806	−2.093
0.30	−0.841	−1.104	−1.313
0.40	−0.356	−0.528	−0.644
0.50	0.127	0	0
0.60	0.653	0.528	0.678
0.70	1.284	1.104	1.456
0.80	2.138	1.806	2.461
0.90	3.585	2.863	4.067
0.95	5.050	3.836	5.615
0.97	6.128	4.529	6.979
0.99	8.506	5.986	9.141
0.995	10.005	6.896	10.897

y	XXV: $A \rightleftarrows B + C + D$ $K = \dfrac{y^3 p^2}{(1 - y)(1 + 2y)^2}$	XXVI: $A + 2B \rightleftarrows C + D + E$ $K = \dfrac{y^3}{4(1 - y)^3}$	XXVII: $2A \rightleftarrows B + 2C$ $K = \dfrac{y^3 p}{(1 - y)^3 (2 + y)}$
	$\log K - 2 \log p = \log M$	$\log K = \log M$	$\log K - \log p = \log M$
0.01	−6.128	−6.5889	−6.2152
0.02	−5.046	−5.6957	−5.226
0.04	−4.2428	−4.7427	−4.4679
0.05	−3.9635	−4.4382	−4.1702
0.10	−3.1126	−3.4531	−3.2306

ν	XXV: $A \rightleftarrows B + C + D$ $K = \dfrac{y^3p^2}{(1-y)(1+2y)^2}$ $\log K - 2\log p = \log M$	XXVI: $A + 2B \rightleftarrows C + D + E$ $K = \dfrac{y^3}{4(1-y)^3}$ $\log K = \log M$	XXVII: $2A \rightleftarrows B + 2C$ $K = \dfrac{y^3p}{(1-y)^2(2+y)}$ $\log K - \log p = \log M$
0.20	—2.2923	—2.3084	—1.9772
0.30	—1.8220	—1.7061	—1.9304
0.40	—1.2552	—1.2144	—1.1303
0.50	—1.2040	—0.6021	—0.6989
0.60	—0.9531	—0.0762	—0.2846
0.70	—0.7022	0.5019	—0.1497
0.80	—0.4217	1.2042	0.6601
0.90	—0.0328	2.2605	1.4002
0.95	0.3093	3.2340	2.0653
0.97	0.5467	3.9270	2.5334
0.99	1.0486	5.3847	3.5111
0.995	1.3430	6.2943	4.119

y	XXVIII: $2A \rightleftarrows B + C + 2D$ $K = \dfrac{y^4p^2}{4(1-y)^2(1+y)^2}$ $\log K - 2\log p = \log M$	XXIX: $3A + B \rightleftarrows C + 2D$ $K = \dfrac{4y^3(4-y)}{27(1-y)^4p}$ $\log K + \log p = \log M$	XXX: $3A \rightleftarrows B + 2C$ $K = \dfrac{4y^3}{27(1-y)^3}$ $\log K = \log M$
0.01	—8.5227	—6.2107	—6.816
0.02	—7.3977	—5.2912	—5.900
0.04	—6.1923	—4.3545	—4.970
0.05	—5.8039	—4.1465	—4.665
0.10	—4.5933	—2.0550	—3.692
0.20	—3.3043	—1.9589	—2.636
0.30	—2.6117	—1.3002	—1.933
0.40	—2.0723	—0.5795	—1.358
0.50	—1.5563	0.0158	—0.829
0.60	—1.1017	0.6284	—0.301
0.70	—0.6367	1.3151	0.275
0.80	—0.1023	2.1811	0.967
0.90	0.6571	3.5247	2.033
0.95	1.3307	4.7921	3.007
0.97	1.8019	5.7041	3.699
0.99	2.7825	7.6361	5.157
0.995	3.3911	8.8459	6.066

19. Activity Coefficient of Individual Gases and Liquids [61]

(a) For $Z_{cr} = 0.23$ (the figures to the left of the dash line are for the liquid state)

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	γ_{sat}	τ_{sat}
0.1	0.0058	0.0763	0.427	0.906	0.944	0.958	0.964	0.970	0.975	0.975	0.975	0.887	0.758
0.2	0.0030	0.0387	0.216	0.719	0.885	0.930	0.940	0.949	0.961	0.989	0.990	0.840	0.819
0.3	0.0020	0.0261	0.146	0.482	0.837	0.897	0.911	0.925	0.941	0.972	0.984	0.806	0.858
0.4	0.0015	0.0198	0.110	0.363	0.796	0.858	0.883	0.905	0.928	0.965	0.975	0.772	0.889
0.5	0.0012	0.0161	0.089	0.294	0.707	0.829	0.854	0.877	0.909	0.951	0.975	0.749	0.914
0.6	0.0010	0.0136	0.075	0.248	0.585	0.800	0.830	0.858	0.896	0.962	0.973	0.727	0.936
0.7	0.0009	0.0118	0.065	0.215	0.503	0.756	0.799	0.832	0.878	0.944	0.968	0.705	0.954
0.8	0.0008	0.0104	0.058	0.190	0.441	0.726	0.774	0.812	0.855	0.920	0.969	0.683	0.971
0.9	0.0007	0.0094	0.052	0.169	0.396	0.688	0.748	0.790	0.845	0.930	0.963	0.664	0.986
1.0	0.0007	0.0086	0.047	0.153	0.360	0.650	0.717	0.767	0.830	0.922	0.957	0.650	1.000
1.1	0.0006	0.0078	0.044	0.146	0.329	0.600	0.686	0.742	0.814	0.922	0.948		
1.2	0.0006	0.0073	0.040	0.136	0.304	0.560	0.663	0.722	0.800	0.910	0.944		
1.3	0.0005	0.0069	0.038	0.127	0.285	0.523	0.629	0.696	0.780	0.910	0.944		
1.4	0.0005	0.0065	0.036	0.119	0.271	0.492	0.600	0.675	0.766	0.897	0.936		
1.5	0.0005	0.0061	0.034	0.113	0.255	0.465	0.570	0.653	0.749	0.890	0.920		
1.6	0.0005	0.0058	0.032	0.107	0.242	0.442	0.546	0.632	0.738	0.895	0.920		
1.7	0.0004	0.0056	0.030	0.102	0.231	0.420	0.525	0.610	0.720	0.895	0.920		

(b) For $Z_{cr} = 0.25$

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	2.0	3.0	γ_{sat}	τ_{sat}
0.1	0.0020	0.0707	0.412	0.957	0.975	0.981	0.985	0.988	0.991	0.995	0.997	0.998	1.000	0.944	0.758
0.2	0.0010	0.0358	0.209	0.761	0.918	0.945	0.955	0.964	0.973	0.987	0.991	0.995	1.000	0.885	0.817

τ\π	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	γ_{sat}	τ_{sat}
0.3	0.0007	0.0210	0.141	0.514	0.865			0.909	0.925	0.938	0.955	0.980	0.986	0.994	1.000	0.838	0.856
0.4	0.0005	0.0144	0.107	0.390	0.813			0.871	0.895	0.913	0.936	0.973	0.982	0.993	1.000	0.803	0.885
0.5	0.0004	0.0155	0.087	0.316	0.722			0.840	0.866	0.888	0.918	0.965	0.978	0.992	1.000	0.775	0.910
0.6	0.0004	0.0126	0.073	0.267	0.609			0.806	0.837	0.863	0.899	0.958	0.974	0.991	1.000	0.749	0.932
0.7	0.0003	0.0110	0.064	0.232	0.529			0.769	0.808	0.839	0.882	0.953	0.972	0.990	1.000	0.727	0.952
0.8	0.0003	0.0098	0.056	0.205	0.469			0.735	0.781	0.816	0.864	0.946	0.967	0.989	1.000	0.703	0.969
0.9	0.0003	0.0088	0.053	0.185	0.423			0.698	0.754	0.791	0.847	0.936	0.963	0.988	1.000	0.680	0.985
1.0	0.0002	0.0080	0.049	0.169	0.385			0.654	0.725	0.768	0.830	0.930	0.959	0.987	1.000	0.654	1.000
1.1	0.0002	0.0074	0.045	0.155	0.355			0.607	0.696	0.745	0.813	0.926	0.955	0.985	1.000	0.638	1.014
1.2	0.0002	0.0069	0.042	0.144	0.330			0.570	0.666	0.721	0.797	0.919	0.951	0.983	1.000	0.625	1.025

(c) For $Z_{or} = 0.27$

τ\π	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	γ_{sat}	τ_{sat}
0.1	0.0102	0.111	0.640	0.961	0.972	0.983	0.985	0.987	0.991	0.993	0.995	0.996	0.997	0.999	1.000	0.946	0.743
0.2	0.0052	0.056	0.325	0.848	0.922	0.947	0.956	0.967	0.974	0.980	0.985	0.987	0.989	0.992	1.000	0.887	0.805
0.3	0.0035	0.038	0.220	0.574	0.871	0.916	0.928	0.942	0.958	0.968	0.976	0.980	0.984	0.989	1.000	0.840	0.846
0.4	0.0027	0.031	0.168	0.437	0.820	0.879	0.899	0.916	0.939	0.955	0.967	0.973	0.980	0.987	1.000	0.805	0.876
0.5	0.0029	0.024	0.136	0.354	0.759	0.846	0.871	0.892	0.920	0.942	0.956	0.966	0.976	0.985	1.000	0.777	0.900
0.6	0.0019	0.020	0.115	0.300	0.642	0.812	0.842	0.867	0.906	0.929	0.944	0.958	0.972	0.983	1.000	0.752	0.928
0.7	0.0016	0.017	0.100	0.261	0.559	0.779	0.816	0.843	0.889	0.917	0.938	0.950	0.968	0.982	1.000	0.730	0.949
0.8	0.0014	0.016	0.089	0.231	0.496	0.745	0.788	0.820	0.872	0.903	0.928	0.944	0.965	0.981	1.000	0.710	0.967
0.9	0.0013	0.015	0.080	0.209	0.448	0.710	0.760	0.796	0.855	0.890	0.920	0.935	0.961	0.980	1.000	0.688	0.984
1.0	0.0012	0.013	0.073	0.191	0.409	0.665	0.731	0.772	0.838	0.878	0.910	0.931	0.957	0.979	1.000	0.665	1.000
1.1	0.0011	0.012	0.068	0.176	0.377	0.618	0.703	0.750	0.821	0.866	0.903	0.923	0.953	0.977	1.000	0.657	1.018
1.2	0.0010	0.011	0.062	0.163	0.351	0.578	0.674	0.726	0.805	0.854	0.892	0.916	0.949	0.975	1.000	0.642	1.032
1.3	0.0010	0.010	0.059	0.153	0.329	0.543	0.645	0.703	0.789	0.842	0.883	0.909	0.945	0.973	1.000	0.628	1.042
1.4	0.0009	0.010	0.056	0.144	0.310	0.513	0.615	0.680	0.773	0.830	0.874	0.901	0.942	0.971	1.000	0.617	1.051
1.5	0.0009	0.009	0.053	0.137	0.293	0.487	0.589	0.658	0.757	0.819	0.866	0.894	0.938	0.970	1.000	0.606	1.062

Appendix 19(c) (concluded)

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	γ_{sat}	τ_{sat}
1.6	0.0008	0.0008	0.050	0.130	0.279	0.464	0.563	0.636	0.741	0.806	0.857	0.888	0.933	0.968	1.00	0.597	1.071
1.7	0.0008	0.0008	0.048	0.124	0.266	0.444	0.540	0.614	0.725	0.794	0.848	0.882	0.929	0.966	1.00	0.588	1.079
1.8	0.0008	0.0008	0.046	0.119	0.255	0.426	0.520	0.594	0.710	0.783	0.840	0.876	0.925	0.964	1.00	0.578	1.087
1.9	0.0007	0.0008	0.044	0.114	0.245	0.410	0.504	0.576	0.695	0.773	0.832	0.870	0.921	0.962	1.00	0.570	1.096
2.0	0.0007	0.0008	0.044	0.110	0.236	0.396	0.485	0.555	0.681	0.762	0.824	0.863	0.918	0.960	0.999	0.562	1.103
2.2	0.0007	0.0008	0.040	0.103	0.221	0.371	0.455	0.527	0.654	0.741	0.808	0.856	0.910	0.956	0.998	0.548	1.116
2.4	0.0006	0.007	0.038	0.097	0.208	0.350	0.432	0.500	0.629	0.721	0.792	0.844	0.903	0.952	0.998	0.536	1.127
2.6	0.0006	0.006	0.036	0.092	0.198	0.333	0.411	0.478	0.606	0.703	0.778	0.833	0.896	0.948	0.997	0.528	1.135
2.8	0.0006	0.006	0.034	0.087	0.189	0.318	0.393	0.460	0.586	0.685	0.765	0.822	0.889	0.946	0.996	0.517	1.144
3.0	0.0006	0.006	0.033	0.084	0.181	0.306	0.378	0.443	0.569	0.669	0.752	0.812	0.882	0.943	0.994	0.509	1.153

(d) For $Z_{cr} = 0.27$

π \ τ	0.9	1	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	4.0	6.0	8.0	10.0	15.0	γ_{sat}	τ_{sat}
1	0.409	0.665	0.772	0.838	0.878	0.910	0.931	0.957	0.979	1.0	1.0	1.0	1.0	1.0	1.0	0.665	1.000
2	0.236	0.396	0.555	0.681	0.762	0.824	0.863	0.918	0.960	0.999	1.0	1.0	1.0	1.0	1.0	0.562	1.103
3	0.181	0.306	0.443	0.569	0.669	0.752	0.812	0.882	0.943	0.994	0.995	0.998	1.001	1.003	1.017	0.509	1.153
3.5	0.166	0.281	0.410	0.526	0.636	0.724	0.788	0.866	0.935	0.991	0.993	0.997	1.001	1.003	1.021	0.491	1.169
4	0.155	0.263	0.385	0.504	0.609	0.700	0.768	0.852	0.929	0.989	0.991	0.996	1.001	1.003	1.029	0.471	1.189
4.5	0.148	0.250	0.366	0.494	0.587	0.682	0.754	0.841	0.923	0.987	0.990	0.995	1.001	1.003	1.029	0.471	1.189
5	0.142	0.240	0.352	0.446	0.570	0.667	0.740	0.832	0.920	0.986	0.989	0.995	1.001	1.003	1.034	0.461	1.199
6	0.135	0.228	0.334	0.445	0.548	0.647	0.722	0.820	0.916	0.986	0.989	0.995	1.001	1.004	1.042	0.449	1.204
7	0.131	0.221	0.325	0.433	0.537	0.637	0.714	0.816	0.918	0.988	0.992	0.998	1.004	1.008	1.049	0.443	1.210
8	0.131	0.219	0.322	0.429	0.533	0.634	0.712	0.817	0.923	0.994	0.999	1.005	1.010	1.015	1.057	0.440	1.216

π																
9	0.132	0.220	0.323	0.430	0.534	0.636	0.716	0.824	0.933	1.004	1.008	1.014	1.018	1.023	1.064	0.440 1.126
10	0.134	0.233	0.325	0.434	0.540	0.643	0.724	0.834	0.947	1.016	1.019	1.024	1.027	1.031	1.071	0.449 1.207
15	0.164	0.265	0.378	0.496	0.616	0.727	0.814	0.933	1.053	1.107	1.096	1.089	1.080	1.074	1.107	0.475 1.182
20	0.222	0.348	0.484	0.620	0.756	0.881	0.976	1.006	1.224	1.242	1.204	1.171	1.148	1.124	1.145	0.530 1.132
25	0.318	0.479	0.648	0.811	0.961	1.103	1.214	1.349	1.455	1.413	1.334	1.266	1.223	1.177	1.183	0.596 1.071
30	0.469	0.679	0.894	1.088	1.248	1.420	1.545	1.688	1.784	1.621	1.476	1.372	1.306	1.224	1.220	0.674 0.987

(e) For $Z_{cr}=0.29$

$\pi \backslash \tau$	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	2.0	3.0	γ_{sat}	τ_{sat}
0.1	0.0509	0.212	0.800	0.966	0.975	0.984	0.987	0.989	0.992	0.995	0.997	0.999	1.000	0.948	0.714
0.2	0.0266	0.113	0.410	0.900	0.936	0.953	0.961	0.968	0.975	0.989	0.992	0.997	1.000	0.890	0.781
0.3	0.018	0.078	0.275	0.730	0.888	0.920	0.934	0.945	0.960	0.982	0.988	0.995	1.000	0.843	0.826
0.4	0.0135	0.058	0.210	0.551	0.840	0.887	0.907	0.922	0.942	0.975	0.984	0.993	1.000	0.807	0.861
0.5	0.015	0.048	0.177	0.448	0.740	0.856	0.879	0.898	0.926	0.969	0.981	0.991	1.000	0.781	0.892
0.6	0.0094	0.041	0.145	0.380	0.697	0.821	0.852	0.876	0.909	0.961	0.976	0.989	1.000	0.766	0.919
0.7	0.0082	0.036	0.126	0.331	0.608	0.790	0.825	0.852	0.892	0.955	0.972	0.988	1.000	0.738	0.942
0.8	0.0074	0.031	0.113	0.295	0.541	0.756	0.796	0.828	0.876	0.948	0.970	0.987	1.000	0.718	0.963
0.9	0.0067	0.028	0.103	0.266	0.489	0.720	0.769	0.806	0.857	0.936	0.965	0.986	1.000	0.698	0.982
1.0	0.0062	0.026	0.093	0.243	0.448	0.677	0.744	0.783	0.840	0.930	0.961	0.985	1.000	0.677	1.000
1.1	0.0061	0.026	0.087	0.225	0.414	0.633	0.713	0.759	0.824	0.923	0.957	0.983	1.000	0.663	1.016
1.2	0.006	0.025	0.080	0.210	0.386	0.590	0.683	0.736	0.808	0.920	0.954	0.981	1.000	0.650	1.028

20. Compression Factors of Individual Gases and Liquids [61]

(a) For $Z_{cr} = 0.23$ (the figures to the left of the dash line are for the liquid state)

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	τ_{sat}	Z^g_{sat}	Z^{lq}_{sat}
0.01	0.0015	0.0013	0.988	0.993	0.997	0.998	0.999	0.999	1.000	1.001	1.001	—	—	—
0.1	0.0150	0.0130	0.0119	0.0114	0.949	0.967	0.973	0.978	0.984	0.995	0.998	0.758	0.886	0.0116
0.2	0.0299	0.0260	0.0238	0.0228	0.886	0.928	0.940	0.951	0.965	0.986	0.992	0.829	0.820	0.0227
0.3	0.0448	0.0389	0.0356	0.0342	0.813	0.888	0.910	0.925	0.946	0.974	0.988	0.858	0.760	0.035
0.4	0.0597	0.0519	0.0474	0.0456	0.721	0.844	0.875	0.898	0.928	0.971	0.984	0.889	0.700	0.047
0.5	0.0745	0.0648	0.0591	0.0568	0.059	0.798	0.842	0.872	0.911	0.966	0.981	0.914	0.650	0.060
0.6	0.0894	0.0776	0.0709	0.0679	0.0706	0.709	0.777	0.822	0.889	0.954	0.973	0.940	0.602	0.0749
0.7	0.104	0.0904	0.0826	0.0790	0.0817	0.680	0.760	0.810	0.871	0.959	0.972	0.954	0.548	0.091
0.8	0.119	0.103	0.0942	0.0900	0.0927	0.605	0.715	0.779	0.848	0.941	0.968	0.971	0.486	0.100
0.9	0.134	0.116	0.106	0.101	0.104	0.515	0.665	0.743	0.831	0.934	0.963	0.986	0.415	0.136
1.0	0.148	0.129	0.117	0.112	0.122	0.232	0.610	0.707	0.810	0.926	0.959	1.000	0.232	0.232
1.1	0.163	0.142	0.129	0.123	0.125	0.163	0.549	0.670	0.789	0.919	0.955			
1.2	0.178	0.154	0.140	0.134	0.135	0.164	0.479	0.629	0.767	0.919	0.951			
1.3	0.192	0.167	0.152	0.144	0.146	0.174	0.400	0.591	0.749	0.907	0.949			
1.4	0.207	0.180	0.163	0.155	0.156	0.182	0.311	0.541	0.721	0.894	0.941			
1.5	0.221	0.192	0.175	0.166	0.167	0.191	0.286	0.504	0.707	0.895	0.952			
1.6	0.236	0.205	0.186	0.177	0.177	0.200	0.262	0.460	0.685	0.883	0.935			
1.7	0.251	0.217	0.196	0.187	0.187	0.209	0.258	0.419	0.652	0.874	0.931			

(b) For $Z_{cr} = 0.25$

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	2.0	3.0	τ_{sat}	Z^g_{sat}	Z^{lq}_{sat}
0.01	0.985	0.987	0.989	0.991	0.993	0.995	0.996	0.996	0.997	0.998	0.998	0.999	1.000	—	—	—
0.1	0.017	0.0145	0.0140	0.912	0.940	0.963	0.971	0.976	0.983	0.991	0.992	0.994	1.000	0.758	0.895	0.014

(continued)

π	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	τ_{sat}	Z^{g}_{sat}	Z^{lq}_{sat}
0.2	0.032	0.028	0.027	0.026	0.884	0.923	0.936	0.948	0.963	0.985	0.989	0.994	1.000	1.000	0.817	0.830	0.028
0.3	0.048	0.043	0.040	0.039	0.822	0.882	0.902	0.919	0.942	0.978	0.980	0.994	1.000	1.000	0.856	0.780	0.040
0.4	0.062	0.057	0.053	0.051	0.745	0.838	0.868	0.889	0.920	0.968	0.984	0.994	1.000	1.000	0.885	0.732	0.052
0.5	0.080	0.071	0.066	0.064	0.068	0.792	0.833	0.860	0.901	0.961	0.978	0.993	1.000	1.000	0.910	0.681	0.069
0.6	0.096	0.086	0.079	0.077	0.080	0.744	0.798	0.831	0.880	0.950	0.971	0.992	1.000	1.000	0.832	0.628	0.086
0.7	0.112	0.100	0.092	0.089	0.092	0.690	0.758	0.800	0.860	0.947	0.974	0.992	1.000	1.000	0.952	0.570	0.103
0.8	0.128	0.114	0.105	0.102	0.105	0.616	0.716	0.766	0.839	0.944	0.970	0.991	1.000	1.000	0.969	0.505	0.124
0.9	0.144	0.128	0.118	0.114	0.117	0.500	0.664	0.731	0.817	0.937	0.967	0.991	1.000	1.000	0.985	0.427	0.152
1.0	0.160	0.142	0.130	0.126	0.129	0.250	0.600	0.694	0.792	0.926	0.963	0.988	1.000	1.000	1.000	0.250	0.250
1.1	0.176	0.156	0.144	0.139	0.142	0.214	0.536	0.654	0.772	0.915	0.958	0.984	1.000	1.000	—	—	—

(c) For $Z_{cr} = 0.27$

τ \ π	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	τ_{sat}	Z^{g}_{sat}	Z^{lq}_{sat}
0.01	0.986	0.988	0.990	0.992	0.994	0.995	0.996	0.997	0.998	0.998	0.998	0.999	0.999	1.000	1.000	—	—	—
0.1	0.018	0.016	0.015	0.921	0.947	0.965	0.971	0.976	0.983	0.987	0.990	0.991	0.992	0.994	1.000	0.743	0.898	0.015
0.2	0.037	0.033	0.030	0.030	0.890	0.927	0.940	0.950	0.965	0.974	0.982	0.986	0.989	0.994	1.000	0.805	0.833	0.030
0.3	0.055	0.049	0.046	0.044	0.826	0.889	0.908	0.923	0.946	0.961	0.972	0.980	0.989	0.994	1.000	0.846	0.783	0.045
0.4	0.073	0.065	0.061	0.059	0.764	0.846	0.873	0.894	0.924	0.945	0.959	0.970	0.984	0.994	1.000	0.886	0.738	0.060
0.5	0.093	0.082	0.076	0.073	0.077	0.801	0.838	0.866	0.905	0.931	0.949	0.963	0.980	0.993	1.000	0.900	0.693	0.077
0.6	0.110	0.098	0.092	0.088	0.091	0.755	0.802	0.837	0.905	0.910	0.937	0.953	0.974	0.992	1.000	0.928	0.641	0.096
0.7	0.128	0.113	0.106	0.102	0.105	0.704	0.766	0.805	0.862	0.900	0.928	0.948	0.974	0.992	1.000	0.949	0.583	0.114
0.8	0.147	0.130	0.121	0.116	0.120	0.640	0.723	0.773	0.840	0.888	0.921	0.945	0.972	0.990	1.000	0.967	0.519	0.136
0.9	0.165	0.147	0.136	0.131	0.134	0.520	0.670	0.738	0.818	0.874	0.912	0.938	0.968	0.990	1.000	0.984	0.443	0.164
1.0	0.183	0.163	0.151	0.145	0.148	0.270	0.611	0.700	0.795	0.857	0.899	0.929	0.964	0.988	1.000	1.000	0.270	0.270
1.1	0.201	0.179	0.165	0.159	0.162	0.224	0.541	0.655	0.773	0.841	0.888	0.918	0.956	0.984	1.000			
1.2	0.220	0.195	0.180	0.173	0.176	0.220	0.478	0.618	0.751	0.827	0.875	0.911	0.951	0.981	1.000			
1.3	0.238	0.211	0.195	0.187	0.190	0.225	0.415	0.574	0.728	0.811	0.865	0.902	0.947	0.981	1.000			

Appendix 20(c) (concluded)

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	τ_{sat}	Z^g_{sat}	Z^{lq}_{sat}
1.4	0.256	0.227	0.210	0.201	0.203	0.234	0.366	0.534	0.705	0.795	0.855	0.894	0.945	0.979	1.000			
1.5	0.274	0.243	0.224	0.215	0.217	0.247	0.332	0.496	0.682	0.783	0.846	0.888	0.940	0.976	0.999			
1.6	0.293	0.259	0.239	0.229	0.230	0.254	0.323	0.455	0.653	0.768	0.837	0.872	0.916	0.974	0.997			
1.7	0.311	0.275	0.254	0.243	0.244	0.268	0.328	0.432	0.638	0.755	0.829	0.877	0.932	0.972	0.997			
1.8	0.329	0.291	0.268	0.257	0.257	0.279	0.332	0.416	0.620	0.742	0.819	0.869	0.929	0.971	0.995			
1.9	0.347	0.307	0.282	0.270	0.270	0.293	0.338	0.408	0.600	0.731	0.812	0.861	0.922	0.969	0.991			
2.0	0.365	0.323	0.297	0.284	0.283	0.306	0.341	0.400	0.573	0.716	0.801	0.852	0.915	0.966	0.986			
2.2	0.402	0.335	0.326	0.311	0.309	0.328	0.358	0.404	0.562	0.697	0.786	0.842	0.908	0.960	0.984			
2.4	0.438	0.387	0.355	0.339	0.335	0.352	0.377	0.413	0.550	0.682	0.776	0.832	0.901	0.956	0.984			
2.6	0.474	0.419	0.384	0.365	0.361	0.375	0.399	0.431	0.540	0.670	0.768	0.824	0.893	0.953	0.984			
2.8	0.540	0.451	0.413	0.392	0.386	0.401	0.421	0.450	0.554	0.666	0.762	0.819	0.890	0.953	0.984			
3.0	0.546	0.482	0.441	0.419	0.411	0.422	0.444	0.474	0.556	0.660	0.755	0.813	0.886	0.946	0.984			

(d) For $Z_{cr} = 0.27$

π \ τ	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	4.0	6.0	8.0	10.0	15.0
1	0.148	0.270	0.700	0.795	0.857	0.899	0.929	0.964	0.988	1.000	1.000	1.000	1.000	1.000	1.000
2	0.283	0.306	0.400	0.573	0.716	0.801	0.852	0.915	0.966	0.986	0.990	0.995	0.998	1.000	1.020
3	0.411	0.422	0.474	0.556	0.669	0.755	0.813	0.886	0.946	0.984	0.988	0.993	0.996	0.998	1.025
3.5	0.471	0.479	0.518	0.582	0.671	0.754	0.813	0.885	0.951	0.985	0.989	0.994	0.997	0.999	1.030
4	0.532	0.536	0.565	0.609	0.687	0.763	0.823	0.883	0.952	0.986	0.990	0.995	0.997	0.999	1.030
4.5	0.592	0.590	0.611	0.649	0.712	0.780	0.829	0.895	0.957	0.989	0.992	0.996	0.998	0.999	1.035
5	0.652	0.645	0.665	0.701	0.749	0.807	0.849	0.908	0.965	0.996	0.997	0.998	0.999	1.000	1.040
6	0.768	0.756	0.768	0.792	0.824	0.863	0.893	0.940	0.993	0.995	0.997	0.999	1.000	1.010	1.045

π	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	2.0	3.0	τ_sat	Z^g_sat
7	0.888	0.865	0.866	0.880	0.904	0.928	0.952	0.990	1.028	1.032	1.035	1.037	1.039	1.042	1.050
8	1.005	0.975	0.970	0.975	0.984	0.996	1.012	1.041	1.070	1.068	1.065	1.064	1.063	1.062	1.061
9	1.119	1.074	1.060	1.057	1.063	1.071	1.081	1.100	1.120	1.107	1.099	1.089	1.082	1.077	1.070
10	1.233	1.193	1.160	1.148	1.144	1.144	1.146	1.154	1.159	1.130	1.120	1.100	1.085	1.080	1.070
15	1.796	1.704	1.631	1.573	1.528	1.496	1.476	1.448	1.400	1.310	1.255	1.200	1.170	1.130	1.100
20	2.341	2.200	2.088	1.995	1.921	1.862	1.818	1.767	1.691	1.500	1.400	1.300	1.250	1.185	1.140
25	2.88	2.69	2.51	2.39	2.27	2.19	2.15	2.09	1.99	1.67	1.53	1.42	1.32	1.24	1.17
30	3.40	3.15	2.93	2.74	2.63	2.56	2.49	2.39	2.24	1.84	1.66	1.50	1.40	1.30	1.20

(e) For $Z_{cr}=0.29$

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	2.0	3.0	τ_sat	Z^g_sat	Z^lq_sat
0.01	0.988	0.990	0.993	0.994	0.995	0.996	0.997	0.998	0.998	0.999	1.000	1.000	1.000	—	—	—
0.1	0.021	0.019	0.018	0.925	0.930	0.969	0.974	0.979	0.984	0.992	0.992	0.994	1.000	—	—	—
0.2	0.042	0.038	0.035	0.854	0.900	0.934	0.946	0.955	0.967	0.986	0.989	0.994	1.000	0.714	0.900	0.018
0.3	0.063	0.056	0.052	0.051	0.840	0.893	0.913	0.927	0.948	0.980	0.989	0.994	1.000	0.781	0.839	0.034
0.4	0.084	0.075	0.070	0.067	0.775	0.852	0.879	0.899	0.931	0.973	0.984	0.994	1.000	0.826	0.790	0.051
0.5	0.105	0.094	0.087	0.084	0.705	0.808	0.845	0.870	0.906	0.965	0.980	0.993	1.000	0.861	0.746	0.068
0.6	0.126	0.112	0.104	0.101	0.103	0.760	0.808	0.840	0.888	0.956	0.977	0.992	1.000	0.892	0.698	0.086
0.7	0.147	0.131	0.121	0.117	0.120	0.710	0.770	0.808	0.864	0.949	0.975	0.992	1.000	0.919	0.650	0.103
0.8	0.168	0.149	0.138	0.133	0.136	0.652	0.727	0.776	0.842	0.946	0.972	0.990	1.000	0.942	0.596	0.125
0.9	0.189	0.168	0.155	0.150	0.153	0.544	0.678	0.742	0.822	0.939	0.968	0.990	1.000	0.963	0.536	0.150
1.0	0.210	0.186	0.171	0.165	0.169	0.290	0.620	0.702	0.799	0.930	0.965	0.988	1.000	0.982	0.460	0.177
1.1	0.231	0.205	0.190	0.182	0.185	0.228	0.551	0.660	0.774	0.921	0.958	0.986	1.000	1.000	0.290	0.290

21. Atomic and Structural Constants for Calculating Critical Parameters According to Lydersen [61]

Atomic and structural groups	Δ_T	Δ_p
$-CH_3$	0.020	0.227
$>CH_2$	0.020	0.227
$\underset{/}{\overset{\backslash}{-}}CH$	0.012	0.210
$>C<$	0.000	0.210
$=CH_2$	0.018	0.198
$=CH-$	0.018	0.198
$=C<$	0.000	0.198
$=C=$	0.000	0.198
$\equiv CH$	0.005	0.153
$\equiv C-$	0.005	0.153
Groups in naphthene compounds:		
$-CH_2-$	0.013	0.184
$>CH$	0.012	0.192
$>C<$	−0.007	0.154
Groups in aromatic compounds:		
$=CH-$	0.011	0.154
$=C<$	0.011	0.154
$=C=$	0.011	0.154
Halogen-containing compounds:		
$-F$	0.018	0.224
$-Cl$	0.017	0.320
$-Br$	0.010	0.500
$-I$	0.012	0.830
Oxygen-containing compounds:		
$-OH$ (alcohols)	0.082	0.06
$-OH$ (phenols)	0.031	−0.02
$-O-$ (non-ring)	0.021	0.16
$-O-$ (in ring)	0.014	0.12
$>C=O$ (non-ring)	0.040	0.29
$>C=O$ (in ring)	0.033	0.2
$H\overset{|}{C}=O$ (aldehydes)	0.048	0.33

Appendix 21 (concluded)

Atomic and structural groups	Δ_T	Δ_p
—COOH (acids)	0.085	0.4
—COO — (esters)	0.047	0.47
>O (except for combinations above)	0.02	0.12
Nitrogen-containing compounds:		
—NH₂	0.031	0.095
>NH (non-ring)	0.031	0.135
>NH (in ring)	0.024	0.09
>N — (non-ring)	0.014	0.17
>N — (in ring)	0.007	0.13
—CN	0.060	0.36
—NO₂	0.055	0.42
Sulphur-containing compounds:		
—SH	0.015	0.27
—S — (non-ring)	0.015	0.27
—S — (in ring)	0.008	0.24
=S	0.003	0.24
Miscellaneous compounds:		
>Si<	0.03	0.54
—B —	0.03	—

22. Contributions for Calculating Critical Parameters According to Forman and Thodos [61]

(a) *Group Contributions* $\Delta a^{2/3}$ *and* $\Delta b^{3/4}$ *for Saturated Aliphatic Hydrocarbons*

n	Type 1		Type 2		Type 3		Type 4	
	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$
1								
2	15 577	11.453						
3	15 216	11.453	13 678	6.262				
4	15 035	11.453	13 678	6.262	12 567	2.064		
5	14 927	11.453	13 678	6.262	11 189	0.886	6 181	—4.937
6	14 854	11.453	13 678	6.262	10 270	0.101	4 980	—6.670

n	Type 1		Type 2		Type 3		Type 4	
	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$
7	14 803	11.453	13 678	6.262	9 614	—0.460	4 123	—7.909
8	14 764	11.453	13 678	6.262	9 122	—0.880	3 480	—8.837
9	14 764	11.453	13 678	6.262	8 739	—1.207	2 979	—9.559
10	14 710	11.453	13 678	6.262	8 433	—1.469	2 579	—10.337
11	14 690	11.453	13 678	6.262	8 182	—1.683	2 252	—10.160
12	14 674	11.453	13 678	6.262	7 974	—1.862	1 979	—11.004
13	14 660	11.453	13 678	6.262	7 797	—2.012	1 748	—11.337
14	14 648	11.453	13 678	6.262	7 646	—2.142	1 550	—11.623
15	14 638	11.453	13 678	6.262	7 514	—2.544	1 379	—11.870

(b) *Contributions for Double and Triple Bonds*

Contribution	$\Delta a^{2/3}$	$\Delta b^{3/4}$
First double bond:		
1-1	—3868	—2.021
2-1	—3154	—1.895
2-2	—2551	—2.009
3-1	—1548	—1.706
3-2	—928	—1.820
3-3	—540	—1.930
Second double bond:		
3-1	—828	—1.259
3-2	—496	—1.343
3_u-1	—1332	—1.745
3_u-2	—1324	—1.862
3_u-3	—1316	—1.979
$3_u \leftarrow$ 2-1	—1687	—1.399
$3_u \leftarrow$ 2-2	—910	—1.485
Triple bond:		
1-1	—4269	—3.680
2-1	—1934	—3.008
2-2	—1331	—3.122

Note. The arrow points away from the carbon atom involved in the formation of unsaturated bonds toward the type of carbon atom adjacent to it; to be used in conjugated systems only.

(c) *Contributions for Naphthenic and Aromatic Compounds*

Contribution	$\Delta a^{2/3}$	$\Delta b^{3/4}$
Carbon type:		
2_n	12 535	5.338
3_n	9 910	0.023
4_n	2 066	−8.094
3_a	11 646	5.991
4_a	11 144	1.043
4_p	11 561	1.634
Contribution for naphthenic ring	2 648	9.073
Contribution for aromatic ring	0	0
Position contribution from multiple substitution:		
Naphthene rings:		
cis-1,2	−427	−0.866
1,3	−2 525	−1.493
trans-1,2	−2 525	−1.493
1,3	−4 195	−2.494
Aromatic rings:		
1-2	−830	−1.253
1-3	−1 597	−0.806
1-4	155	0.212
1-5	279	0.254
1-6	488	0.525

Note. If several naphthenic rings are present in the same molecule, a "ring" contribution for each is to be made. If there is only a single substitution in the ring, no position contribution is necessary. Disubstitutions of the form (1,1), (1,4), (1,5), etc. are not defined, but it is recommended that the (1,3) contributions be used in these cases. Also trisubstitutions are undefined, but they may be approximated by using the disubstitution rules and proceeding around the molecule in a clockwise direction. Thus, there would be three disubstitution contributions for a trisubstituted molecule, etc. For example the cyclohexane homologue
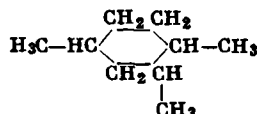
would have a (1,2), a (1,3), and a (1,4) [for the last, as explained above, we use the (1,3) values] disubstitution contributions.

(d) *Constants of Equations for Calculating Group Contributions for Organic Compounds According to Forman and Thodos Method*

Contribution	Functional group	$\Delta a^{2/3} = \dfrac{q}{n} + k$		$\Delta b^{3/4} = \dfrac{s}{n} + t$	
		q	k	s	t
Alcohols	—OH	30 200	14 000	8.96	7.50
Phenols	—OH	0	8 500	0	4.19
Esters:					
non-cyclic	—O—	14 500	6 500	0	3.26
cyclic	—O—	0	9 440	0	2.74
Ketones	—C=O	62 800	16 700	27.20	4.55
Carboxylic acids	—COH ‖ O	142 670	16 730	66.80	5.10
Acid anhydrides	—COC— ‖ ‖ O O	0	43 880	0	14.78
Esters:					
formates	$\overset{O}{\overset{\diagup}{HCO}}$—	35 140	26 800	2.29	15.80
others	—CO— ‖ O	37 430	25 500	—3.00	12.20
Amines:					
primary	—NH₂	4 800	18 900	0	10.15
secondary	—NH	51 800	0	19.60	—1.10
tertiary	—N<	60 200	—4 300	29.20	—7.90
Nitriles	—CN	86 000	25 900	39.70	12.10
Halides in aliphatic chain:					
fluorides:	—F				
first		2 420	12 240	—3.70	10.92
second		—38 500	4 510	—48.50	12.86
third		0	3 450	0	6.92
chlorides:	—Cl				
first		0	22 580	0	11.54
second		66 000	—5 100	19.00	3.90
third		—60 250	29 100	—40.80	19.40
fourth		0	16 500	0	11.46

Contribution	Functional group	$\Delta a^{2/3} = \dfrac{q}{n} + k$		$\Delta b^{3/4} = \dfrac{s}{n} + t$	
		q	k	s	t
bromides:	— Br				
first		2 720	23 550	—4.35	11.49
second		0	20 860	0	5.37
iodide:	— I				
first		0	33 590	0	13.91
Halides in aromatic ring:					
fluoride	— F	0	4 210	0	7.22
chloride	— Cl	0	17 200	0	10.88
bromide	— Br	0	24 150	0	12.74
iodide	— I	0	34 780	0	15.22

23. Change in Enthalpy of Gases and Liquids upon Compression $\dfrac{H^\circ - H}{T_{cr}}$, cal/mol·K [61]

(a) For $Z_{cr} = 0.23$ (the figures to the left of the dash line are for the liquid state)

π\τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	τ_{sat}	$\left(\frac{H^\circ-H}{T_{cr}}\right)^{lq}$	$\left(\frac{H^\circ-H}{T_{cr}}\right)^{g}$
0.1	15.830	14.845	13.810	0.601	0.362	0.252	0.220	0.193	0.155	0.091	—	0.758	13.193	0.758
0.2	15.817	14.834	13.801	12.674	0.796	0.536	0.458	0.397	0.311	0.172	0.133	0.819	12.48	1.275
0.3	15.805	14.825	13.796	12.676	1.349	0.850	0.714	0.614	0.477	0.265	0.205	0.858	11.912	1.760
0.4	15.794	14.814	13.788	12.677	2.053	1.200	0.993	0.843	0.646	0.356	0.284	0.889	11.747	2.210
0.5	15.781	14.804	13.780	12.676	11.271	1.591	1.289	1.081	0.818	0.450	0.340	0.914	11.035	2.732
0.6	15.768	14.793	13.773	12.675	11.309	2.116	1.670	1.384	1.033	0.549	0.421	0.936	10.64	3.239
0.7	15.757	14.783	13.765	12.674	11.324	2.587	1.986	1.618	1.185	0.640	0.479	0.954	10.21	3.740
0.8	15.743	14.772	13.757	12.672	11.343	3.001	2.330	1.833	1.376	0.770	0.543	0.971	9.753	4.400
0.9	15.739	14.761	13.750	12.671	11.354	4.149	2.836	2.225	1.568	0.829	0.617	0.986	9.261	5.156
1.0	15.717	14.750	13.740	12.671	11.379	7.478	3.368	2.574	1.777	0.943	0.688	1.000	7.478	7.478
1.1	15.713	14.744	13.732	12.634	11.394	9.104	3.992	2.946	1.987	1.025	0.771			
1.2	15.695	14.732	13.723	12.628	11.405	9.318	4.756	3.349	2.205	1.161	0.837			
1.3	15.681	14.719	13.715	12.625	11.416	9.502	5.770	3.803	2.433	1.220	0.870			
1.4	15.682	14.709	13.707	12.622	11.425	9.625	5.841	3.834	2.448	1.228	0.902			
1.5	15.655	14.698	13.700	12.614	11.436	9.693	7.514	4.781	2.909	1.414	1.363			

(b) For $Z_{cr} = 0.25$

π\τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	2.0	τ_{sat}	$\left(\frac{H^\circ-H}{T_{cr}}\right)^{lq}$	$\left(\frac{H^\circ-H}{T_{cr}}\right)^{g}$
0.1	15.75	14.79	13.60	0.50	0.36	0.26	0.22	0.185	0.14	0.09	0.06	0.03	0.758	12.68	0.55
0.2	15.80	14.80	13.60	12.06	0.73	0.52	0.44	0.37	0.28	0.14	0.11	0.07	0.817	11.85	0.92

(continued)

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.3	1.4	1.5	τ_{sat}	$\left(\dfrac{H°-H}{T_{cr}}\right)q$	$\left(\dfrac{H°-H}{T_{cr}}\right)g$
0.3	15.75	14.82	13.60	12.07	1.41	0.79	0.66	0.55	0.42	0.22	0.17	0.10	0.856	11.30	1.30
0.4	15.75	14.81	13.60	12.08	1.62	1.10	0.95	0.81	0.62	0.30	0.21	0.13	0.885	10.80	1.71
0.5	15.72	14.81	13.62	12.09	10.51	1.45	1.21	1.02	0.77	0.41	0.29	0.17	0.910	10.31	2.41
0.6	15.71	14.80	13.62	12.10	10.53	1.82	1.52	1.30	1.00	0.50	0.35	0.22	0.932	9.85	2.55
0.7	15.70	14.79	13.61	12.10	10.57	2.23	1.82	1.55	1.18	0.62	0.44	0.28	0.952	9.46	3.08
0.8	15.70	14.78	13.62	12.10	10.61	3.01	2.30	1.87	1.43	0.72	0.51	0.32	0.969	8.97	3.70
0.9	15.70	14.78	13.64	12.20	10.64	3.75	2.69	2.17	1.63	0.82	0.59	0.39	0.983	8.46	4.50
1.0	15.68	14.78	13.66	12.20	10.67	6.50	3.18	2.46	1.86	0.93	0.64	0.43	1.00	6.50	6.50
1.1	15.66	14.78	13.50	12.12	10.67	6.80	3.80	2.87	2.05	1.05	0.72	0.49			
1.2	15.65	14.78	13.50	12.16	10.71	7.55	4.50	3.24	2.35	1.21	0.82	0.53			

(c) For $Z_{cr} = 0.27$

π \ τ	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	τ_{sat}	$\left(\dfrac{H°-H}{T_{cr}}\right)q$	$\left(\dfrac{H°-H}{T_{cr}}\right)g$
0.1	14.81	13.75	12.52	0.38	0.30	0.23	0.19	0.16	0.13	0.11	0.10	0.08	0.06	0.03	0.03	0.743	12.08	0.43
0.2	14.82	13.76	12.53	11.36	0.64	0.48	0.41	0.36	0.27	0.21	0.17	0.14	0.10	0.06	0.06	0.805	11.28	0.81
0.3	14.82	13.76	12.54	11.37	1.00	0.74	0.62	0.53	0.40	0.32	0.26	0.21	0.16	0.10	0.10	0.846	10.79	1.15
0.4	14.82	13.76	12.55	11.38	1.48	1.00	0.85	0.74	0.56	0.42	0.34	0.28	0.21	0.13	0.12	0.876	10.34	1.52
0.5	14.82	13.76	12.55	11.39	9.90	1.32	1.12	0.97	0.75	0.60	0.48	0.38	0.28	0.17	0.13	0.900	9.86	1.91
0.6	14.82	13.77	12.56	11.30	9.90	1.66	1.40	1.20	0.93	0.73	0.59	0.48	0.35	0.22	0.15	0.928	9.38	2.28
0.7	14.82	13.77	12.56	11.30	9.90	2.08	1.71	1.45	1.13	0.92	0.74	0.60	0.42	0.28	0.16	0.948	8.88	2.74
0.8	14.82	13.77	12.56	11.30	9.91	2.63	2.10	1.76	1.33	1.06	0.85	0.70	0.49	0.32	0.17	0.967	8.29	3.24
0.9	14.81	13.77	12.56	11.40	9.92	3.28	2.56	2.11	1.56	1.21	0.97	0.78	0.56	0.39	0.18	0.984	7.54	4.02
1.0	14.81	13.77	12.56	11.40	9.94	5.80	3.10	2.42	1.78	1.40	1.13	0.91	0.63	0.43	0.19	1.00	5.80	5.80
1.1	14.80	13.77	12.55	11.40	9.98	7.36	3.73	2.79	2.02	1.58	1.28	1.04	0.70	0.48	0.20			
1.2	14.80	13.76	12.54	11.40	10.03	7.68	4.30	3.12	2.25	1.74	1.43	1.17	0.80	0.52	0.22			

Appendix 21(c) (concluded)

τ / π	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	τ_sat	$\left(\frac{H^o-H}{T_{cr}}\right)^{lg}$	$\left(\frac{H^o-H}{T_{cr}}\right)^{g}$
1.3	14.80	13.76	12.54	11.40	10.08	8.00	4.84	3.47	2.47	1.93	1.54	1.24	0.88	0.56	0.23			
1.4	14.80	13.76	12.53	11.40	10.12	8.16	5.56	3.88	2.68	2.08	1.65	1.35	0.96	0.60	0.24			
1.5	14.80	13.75	12.52	11.40	10.16	8.24	6.16	4.28	2.89	2.23	1.79	1.46	1.03	0.66	0.26			
1.6	14.80	13.75	12.52	11.40	10.20	8.32	6.65	4.63	3.12	2.42	1.91	1.58	1.10	0.70	0.27			
1.7	14.80	13.74	12.52	11.40	10.24	8.47	6.96	4.92	3.39	2.56	2.04	1.67	1.18	0.75	0.29			
1.8	14.80	13.73	12.51	11.40	10.26	8.55	7.16	5.22	3.56	2.68	2.16	1.80	1.26	0.79	0.30			
1.9	14.80	13.72	12.50	11.39	10.28	8.63	7.36	5.57	3.78	2.84	2.30	1.88	1.33	0.84	0.31			
2.0	14.80	13.72	12.49	11.38	10.29	8.69	7.48	5.72	4.00	3.05	2.38	1.93	1.39	0.88	0.32			
2.2	14.79	13.69	12.45	11.37	10.30	8.74	7.59	6.01	4.32	3.34	2.62	2.13	1.54	0.97	0.34			
2.4	14.78	13.66	12.42	11.36	10.31	8.78	7.70	6.29	4.64	3.62	2.86	2.33	1.63	1.07	0.36			
2.6	14.77	13.62	12.39	11.35	10.32	8.82	7.81	6.57	4.96	3.90	3.10	2.53	1.75	1.17	0.38			
2.8	14.77	13.60	12.36	11.34	10.34	8.87	7.92	6.85	5.28	4.19	3.34	2.73	1.87	1.26	0.40			
3.0	14.76	13.58	12.33	11.32	10.30	8.91	8.04	7.13	5.60	4.47	3.58	2.92	1.98	1.35	0.43			

(d) For $Z_{cr}=0.27$

τ / π	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.7	2.0	3.0	4.0	6.0	8.0	10.0	15.0
1.0	9.94	5.80	2.42	1.78	1.40	1.13	0.91	0.63	0.43	0.19	—	—	—	—	—
2.0	10.29	8.69	5.72	4.0	3.05	2.38	1.93	1.39	0.88	0.32	0.11	0.02	0.01	0.00	0.03
3.0	10.30	8.91	7.13	5.60	4.47	3.58	2.92	1.98	1.35	0.43	0.20	0.04	0.01	0.00	0.07
3.5	10.28	8.99	7.33	5.92	4.82	3.92	3.24	2.22	1.55	0.48	0.24	0.05	0.01	0.00	0.08
4.0	10.26	9.08	7.53	6.24	5.18	4.26	3.50	2.45	1.76	0.53	0.28	0.06	0.02	0.00	0.09
4.5	10.24	9.11	7.64	6.42	5.38	4.47	3.75	2.62	1.90	0.57	0.31	0.08	0.02	0.00	0.10
5.0	10.22	9.13	7.76	6.60	5.58	4.68	3.90	2.80	2.05	0.61	0.34	0.10	0.03	0.00	0.11

π	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	2.0	τ_{sat}	$\left(\frac{H°-H}{T_{cr}}\right)^{lq}$	$\left(\frac{H°-H}{T_{cr}}\right)^{g}$
6.0	10.44	9.17	7.88	6.78	5.82	4.94	4.17	3.08	2.28	0.65	0.35	0.14	0.03	0.00	0.13
7.0	10.08	9.15	7.92	6.86	5.98	5.10	4.36	3.27	2.43	0.66	0.35	0.14	0.03	0.00	0.15
8.0	10.02	9.12	7.91	6.89	5.98	5.10	4.36	3.32	2.54	0.67	0.19	0.05	0.02	0.00	0.16
9.0	9.93	9.02	7.90	6.84	5.94	5.11	4.42	3.37	2.56	0.66	0.16	0.05	0.02	0.00	0.17
10.0	9.83	9.02	7.90	6.86	5.96	5.18	4.48	3.44	2.62	0.63	0.14	0.04	0.02	0.00	0.17
15.0	9.32	8.57	7.41	6.44	5.64	4.95	4.30	3.30	2.47	0.27	−0.02	−0.03	−0.02	0.00	0.15
20.0	8.74	8.06	6.94	6.00	5.16	4.44	3.78	2.80	1.98	−0.25	−0.23	−0.14	−0.07	0.00	0.14
25.0	8.12	7.49	6.53	5.59	4.77	4.04	3.39	2.32	1.35	−0.90	−0.71	−0.27	−0.14	0.00	0.10
30.0	7.58	6.94	5.92	5.00	4.18	3.45	2.80	1.80	0.94	−1.78	−1.48	−0.48	−0.21	−0.13	0.07

(e) For $Z_{cr}=0.29$

τ \ π	0.5	0.6	0.7	0.8	0.9	1.0	1.05	1.1	1.2	1.5	1.7	2.0	τ_{sat}	$\left(\frac{H°-H}{T_{cr}}\right)^{lq}$	$\left(\frac{H°-H}{T_{cr}}\right)^{g}$
0.1	11.20	10.76	10.07	0.34	0.25	0.18	0.15	0.13	0.10	0.07	0.05	0.03	0.714	10.04	0.43
0.2	11.20	10.76	10.12	0.67	0.50	0.36	0.30	0.25	0.19	0.13	0.10	0.07	0.781	9.6	0.66
0.3	11.20	10.76	10.12	9.46	0.75	0.53	0.44	0.37	0.29	0.19	0.15	0.10	0.826	9.29	1.04
0.4	11.20	10.76	10.12	9.46	1.20	0.80	0.66	0.57	0.45	0.26	0.19	0.13	0.861	8.93	1.35
0.5	11.15	10.77	10.12	9.46	1.64	1.10	0.93	0.80	0.64	0.36	0.27	0.17	0.892	8.58	1.70
0.6	11.12	10.77	10.15	9.60	9.03	1.41	1.17	1.02	0.82	0.43	0.32	0.22	0.919	8.24	2.04
0.7	11.09	10.77	10.18	9.60	8.97	1.76	1.45	1.25	1.01	0.56	0.41	0.28	0.942	7.95	2.45
0.8	11.02	10.70	10.23	9.72	8.93	2.30	1.79	1.48	1.18	0.66	0.47	0.32	0.963	7.58	2.93
0.9	11.00	10.65	10.25	9.74	8.90	3.09	2.17	1.75	1.37	0.74	0.54	0.39	0.982	7.15	3.61
1.0	10.99	10.63	10.25	9.77	8.96	5.40	2.63	2.05	1.55	0.87	0.60	0.43	1.00	5.40	5.40
1.1	10.95	10.62	10.40	9.95	9.00	6.00	3.21	2.37	1.78	0.99	0.69	0.47			
1.2	10.93	10.61	10.45	10.00	9.10	6.40	4.13	2.72	2.07	1.11	0.76	0.51			

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Answers to Problems

Chapter 1

1. —1419.61 kJ. **2.** 5.53 $\times$ 10^5 kJ. **3.** —80.9 kcal. **4.** —29 000, 21 000, 30 000, and —39 000 cal. **5.** —123 900 cal/mol. **6.** —92 690 cal/mol. **7.** —24.6 kcal. **8.** —820.33 kcal/mol. **10.** —54.060 kcal. **11.** 1850 cal. **14.** (a) 11.715; (b) —107.155; (c) —85.563; and (d) 8.279 (all in kcal/mol). **15.** —65.6 kJ. **16.** 120.9 kJ. **18.** 10.858 kcal. **19.** —1553 kcal. **20.** —4757 kcal. **23.** No, it may not, because $\Delta H - \Delta U = 0.546$ kcal, which is beyond the limits of the accuracy of determining the heats of combustion of C and CO **24.** —18 760 and —18 178 cal/mol. **26.** $(\Delta H^\circ_{298})_{vap} = 10.519$ kcal/mol. **27.** —11.21 kcal. **32.** —442.8 and —895.2 kcal/mol. **35.** $(\Delta H^\circ_{298})^g_{comb} = -1474.08$, $(\Delta H^\circ_{298})^{lq}_{comb} = -1463.76$, and $(\Delta H^\circ_{298})_{form} = -55.56$ kcal/mol. **36.** (a) —1473.86; (b) —1466.76; (c) —1710.74; (d) —1510.55; and (e) —1317.39 kcal/mol. **37.** (a) —4.02; and (b) —4.02 kcal. **38.** —620.74 kcal/mol. **39.** —633.00 kcal/mol. **40.** —18.28 kcal/mol. **41.** 7.47 and 7.87 kcal/mol. **43.** —101 600 and —96 000 cal/mol. **44.** —12.2 kcal. **45.** 17.4 kcal. **46.** 1.2 kcal. **47.** —53.590 and —53.629 kcal/mol. **50.** —62.412 kcal/mol. **51.** (a) —25.1; and (b) —97.8 kcal/mol. **54.** —51.8 kcal/mol. **55.** (a) —11.81; (b) —52.87; (c) —0.14; and (d) 61.04 kcal/mol. **58.** (1) —77; (2) —34; (3) 7; (4) —28; (5) —114; (6) —36; and (7) —73 kcal/mol. **59.** —1289.1, —1527.1, and —2003.95 kcal/mol. **60.** (1) —39.944; (2) —44.606; (3) 19.80; (4) —29.556; (5) —9.898; (6) —11.95; (7) —20.83; and (8) —11.256 kcal/mol. **61.** 56.82 kcal. **62.** —23.63 kcal. **63.** $\Delta H^\circ_0 = -2.727$, $\Delta H^\circ_{298} = -1.324$, and $\Delta H^\circ_{400} = -2.387$ kcal. **64.** $\Delta H^\circ_{298} = -19.658$, $\Delta H^\circ_{400} = -19.429$, $\Delta H^\circ_{500} = -19.170$, $\Delta H^\circ_{600} = -19.170$, $\Delta H^\circ_{800} = -18.370$, and $\Delta H^\circ_{1000} = -17.850$ kcal. **65.** —43.8 kcal/mol. **66.** —55.69 kcal/mol. **67.** 18.58 kcal/mol. **68.** 35.20 kcal/mol. **69.** (1) —44.87, —44.82, —44.85; (2) —48.39, —46.82, —48.39; (3) —30.01, —29.46, —29.46; (4) 44.32, 44.39, 44.64; (5) —0.05, —0.06, 0.08; and (6) 4.1, 4.12, 4.18 kcal/mol. **71.** (1) +0.17, +0.80, +0.30 and —0.96, —1.22, +0.36; (2) —0.01, 0, —0.01 and —0.70, +0.45, +0.81; and (3) +0.01, +0.01, 0 and +0.43, +1.46, +3.18 kcal/mol. **72.** 17.75 cal.

73. 16 700|cal. **74.** 32.98 kJ/kmol·K, 1.03 kJ/kg•K, and|1.472|kJ/m³·K.
75. 1.3376 kJ/m³·K. **76.** 8.449 cal/mol·K. **77.** $n = 1.02$, and $\bar{C}_p =$
$= 93.2$ cal/mol·K. **78.** 34.67 J/mol·K. **79.** 156.33 J/mol·K.
80. 37.99 J/mol·K. **81.** $\bar{C}_p = 30.336$ J/mol·K, and $C_p = 28.644 +$
$+ 2.82 \times 10^{-3}T$. **82.** $C_p = -3.10 + 19.36 \times 10^{-3}T - 11.60 \times$
$\times 10^{-6}T^2$. **83.** $C_p^{\circ} = 3.705 + 1.655 \times 10^{-2}T - 0.0275 \times 10^{-4}T^2$.
85. 10.499, 11.973, 12.967, 13.728, 14.366, 14.366, 14.933, 15.449,
15.922, 16.353, 16.744, 17.099, 17.418, and 17.704 cal/mol·K.
86. 18.59 cal/mol·K. **87.** (1) 12.658; (2) 11.813; (3) 10.371; and
(4) 14.192 cal/mol·K. **89.** 0.04, −1.28, −2.05, −2.85, and
−4.38 cal/mol·K. **90.** 54.25 cal/mol·K.
91. (In cal/mol·K):

(1) $C_p^{\circ} = -7.875 - 27.52 \times 10^{-3}T - 117.838 \times 10^{-6}T^2$

(2) $C_p^{\circ} = 4.168 + 191.486 \times 10^{-3}T - 104.551 \times 10^{-6}T^2$|

(3) $C_p^{\circ} = 0.530 + 209.378 \times 10^{-3}T - 113.282 \times 10^{-6}T^2$

(4) $C_p^{\circ} = 0.0447 + 221.272 \times 10^{-3}T - 117.927 \times 10^{-6}T^2$

(5) $C_p^{\circ} = -14.214 + 252.06 \times 10^{-3}T - 143.285 \times 10^{-6}T^2$|

92. (In cal/mol·K):

(1) $C_p^{\circ} = -6.401 + 91.18 \times 10^{-3}T - 25.344 \times 10^{-6}T^2 +$
$+ 9e^{-0.007T}$

(2) $C_p^{\circ} = -13.34 + 235.2 \times 10^{-3}T - 88.75 \times 10^{-6}T^2 +$
$+ 84e^{-0.007T}$

(3) $C_p^{\circ} = -5.091 + 124.7 \times 10^{-3}T - 46.917 \times 10^{-6}T^2 +$
$+ 2.55e^{-0.007T}$

(4) $C_p^{\circ} = -0.557 + 114.77 \times 10^{-3}T - 59.763 \times 10^{-6}T^2$|

(5) $C_p^{\circ} = -0.0447 + 221.27 \times 10^{-3}T - 117.93 \times 10^{-6}T^2$

93. $C_p^{\circ} = 2.25 + 168.93 \times 10^{-3}T - 63.15 \times 10^{-6}T^2$, and $C_{p,\ 442}^{\circ} =$
$= 65.60$ cal/mol·K (2.13%). **94.** (1) $C_p^{\circ} = 6.72 + 41.73 \times 10^{-3}T -$
$- 10.37 \times 10^{-6}T^2$; (2) 20.81 and 23.58 cal/mol·K; and (3) 4378 cal.
95. $C_p^{\circ} = -1.96 + 145.94 \times 10^{-3}T - 56.92 \times 10^{-6}T^2$, and $C_{p,\ 1000}^{\circ} =$
$= 87.06$ cal/mol·K. **96.** 10.3 kcal/mol. **97.** −10.767 kcal•
98. 7093 cal/mol. **99.** −150 815 cal. **100.** $\Delta H_T^{\circ} = 43\ 000 + 0.04T +$
$+ 5 \times 10^{-6}T^2 + 0.62 \times 10^5 T^{-1}$. **101.** −0.0045 cal/K. **102.** −26 300
and −23 200 cal. **103.** $C_{p\ (CaCO_3)} = 19.46 + 1.24 \times 10^{-3}T - 1.0 \times$
$\times 10^5 T^{-2}$. **104.** −21 530 cal. **107.** 1420 K. **108.** The heat of the
reaction will diminish with increasing temperature (its absolute
value will grow, because in the given case $\Delta H < 0$); the rate of
diminishing will become smaller, because the absolute value of ΔC_p
diminishes with increasing temperature. **109.** 590 K. **110.** (In cal):

(a) $\Delta H_T^{\circ} = -30\ 703 - 1.867T + 64.1 \times 10^{-3}T^2 + 71.66 \times$
$\times 10^{-6}T^3$

(b) $\Delta H_T^{\circ} = -22\ 703 + 6.83T - 35.25 \times 10^{-3}T^2 + 10.3 \times$
$\times 10^{-6}T^3$

111. $\Delta H_T = -17\ 660R - 8.82RT + 0.006\ 85RT^2$. 112. $\Delta H_{400} = -14\ 300$ cal. 113. $-194\ 000$ cal. 114. $-200\ 40$ cal. 115. $\Delta H = -7740$ cal (4.1%). 116. $\Delta H_T^\circ = -43\ 880 - 19.71T + 0.010\ 45T^2$, and $\Delta H_{298}^\circ = -48\ 830$ cal.

Chapter 2

117. 9.14 cal/mol·K. 118. 8.72 cal/mol·K. 119. 2000 dm³. 120. 0.326 cal/K. 121. 5.15 cal/K. 122. -23.66 cal/K. 123. 3.713 cal/mol·K. 124. -0.31 cal/K. 125. 365 K. 126. 1032 J/K. 127. 17.307 J/K. 128. 1.64 times. 129. 54.1 (49.77) and 36.7 (34.43) cal/mol·K. 131. 7.4 cal/K. 136. -36.9 cal/mol·K. 137. -28.256 cal/mol·K. 138. 29.8 cal/mol·K. 139. 5.63 J/K or 1.34 cal/K. 140. (a) 1.04; and (b) 0.575 cal/K. 142. 16.31 cal/mol·K. 143. $(\partial S/\partial p)_{t=100} = -0.001\ 836$ cal/mol·atm·K. 145. 42.8 cal/mol·K. 147. $(\partial S/\partial V)_T = 34.65$ mm Hg/K. 148. $(\partial S/\partial T)_p = 0.034$. 149. 0.826 cal/mol·K. 150. 50.86 cal/mol·K. 151. $(\partial S/\partial T)_p = 5.94 \times 10^{-4}$. 152. 17. 156. 48.07 cal/mol·K. 157. 84.5 cal/mol·K. 159. 92.5, 101.8, 64.3, 76.4, and 84.3 cal/mol·K. 164. (a) 6.38; (b) 14.79; (c) 10.8; (d) 20.34; (e) 16.60; (f) 23.07; (g) 27.20; (h) 33.99; (i) 21.61; (j) 28.51; (k) 18.36; (l) 24.40 cal/mol·K. 166. (a) -38.996; (b) 4.737; (c) -4.88; (d) -38.7; (e) -13.13; and (f) 45.32 cal/K. 167. $\Delta S_T^\circ = -53.243 + 10.751 \ln T - 22.092 \times 10^{-3}T - 2.636 \times 10^{-6}T^2$. 168. -20.21 cal/K. 169. $\Delta S_T^\circ = -86.69 - 28.92 \ln T + 50.213 \times 10^{-3}T - 10.57 \times 10^{-6}T^2$.

Chapter 3

173. In the forward direction. 174. No, it will not. 175. In the forward direction. 176. Yes, it will. 177. (1) In the forward direction; and (2) it will proceed in the reverse direction. 178. Yes, it will. 179. No, it will not. 180. In the forward direction, i.e. Zn will dissolve and Fe will be liberated. 181. Yes, it will. 182. The current will flow from the Zn to the Cu; the work is 47 200 cal. 183. 4860 cal. 184. Reactions 4 ($\Delta G_{298}^\circ = 200$ cal), 5 ($\Delta G_{298}^\circ = -19\ 700$ cal), 6 ($\Delta G_{298}^\circ = -7450$ cal), and 8 ($\Delta G_{298}^\circ = -19\ 700$ cal) are possible. 185. The reaction is possible; $\Delta G_{800}^\circ = -191\ 500$ cal. 186. No, it is not. 187. $\Delta G_{700}^\circ = -14\ 000$ cal. 188. 4050 cal; 6.95 atm. 189. 4090 cal. 190. $\Delta G_{298}^\circ = 2537 \pm 1079$ cal, and $K_p = 0.0441 \pm 0.0419$. 192. In the forward direction. 193. No, it does not. 195. 2400 cal. 196. The possibility of the reactions diminishes in the following sequence: $6 > 1 > 2 > 3 > 4 > 5$. 197. Reactions 1, 2, 4, and 9 are possible within the interval from 298 to 1000 K; 5 and 6 are impossible within this interval; reaction 3 is possible below 550 K, 7—below 400 K, 8—below 768 K, 10—below 678 K, and 11—above 507 K.

198. 1460 K. **200.** The temperature dependence of $(\Delta G_T^\circ)_{\text{form}}$ for all the reactions obeys the equation $(\Delta G_T^\circ)_{\text{form}} = A + B \times 10^{-2}T$. The coefficients A and B for the reactions are as follows:

Reaction No. .	1	2	3	4	5	6
A	41.551	51.536	−20.509	−27.386	−132.215	−12.7
B	6.481	4.042	7.83	22.488	17.776	18.358
Reaction No. .	7	8	9	10	11	12
A	16.289	36.628	−187.729	36.277	44.092	11.644
B	14.728	8.937	15.182	10.567	8.87	11.693
Reaction No. .	13	14	15	16		
A	52.779	4.021	−9.112	−178.531		
B	5.918	14.501	6.429	12.017		

201. 19.511 kcal/mol. **202.** Below 1000 K.

Chapter 4

203. (The mole per cent of one of the products is indicated)
(1) 24.8% of $C_6H_5CH_3$; (2) 1.9% of C_7H_{16}; (3) 27.2% of C_7H_{16};
(4) 63.5% of $C_6H_5C_3H_7$; (5) 80.0% of H_2; (6) 96.5% of C_9H_{12}; (7) 2.5%
of iso-C_3H_7OH; (8) 39.8% of CH_3COCH_3; (9) 47.6% of C_4H_9Cl;
(10) 87% of $C_2H_4Cl_2$; (11) 9.6% of HCN; (12) 0.2% of $(CH_3)_2CHCHO$;
(13) 95% of $C_{10}H_{20}$; (14) 27.0% of $CH_3COOC_2H_5$; and (15) 20.8% of
C_4H_6. **204.** (1) 8.4; (2) 100; and (3) 0 (in mole %). **205.** 23.5 mole %.
206. 33 mole %. **207.** 50 mole %. **208.** 3.36 mole %. **209.** 100 mole %
of the product. **210.** 100 mole %. **211.** 0. **212.** 0.0475 atm. **213.** 0.674.
214. 32 mole %. **215.** 2.1 mole %. **217.** 10.69 mole %. **218.** 32.1 mole
% of ketone, and 66 mole % of hydrogen. **219.** 0.2 mole %.
220. 8.85 mole %. **221.** 22.4 mole % of *ortho*-, 21.5% of *para*-, and
47.8 mole % of *meta*-xylene, the remainder being ethylbenzene.
222. 1.44 mole % of 1,1-dimethyl-, 14.2% of 1,2-*cis*-dimethyl-,
and 6.32 mole % of 1,3-*trans*-dimethylcyclopentane, the remainder
being methylcyclopentane. **223.** 2.5 mole % of 1,4-pentadiene,
and 47.2% of 2-methyl-1,3-butadiene, the remainder being 1,3-pen-
tadiene. **224.** 4.5 mole % of *para*-, 10.1% of *meta*-, 4.1% of *ortho*-
xylene, and 0.9 mole % of ethylbenzene. **225.** 48.7 mole % of all the
isomers of C_4H_8. **226.** 46.6 mole % of C_3H_8, 35.4% of H_2, 4% of
propadiene, and 14 mole % of methylacetylene. **227.** 0.4 mole %
each of $C_{12}H_{26}$ and H_2, 19.6% each of C_6H_{14}, C_5H_{12}, and C_7H_{16},
and 20.2 mole % each of C_4H_{10} and C_8H_{18}. **228.** 14 mole % each
of CH_4 and C_9H_{20}, 9.6% each of C_5H_{12} and C_7H_{16}, 9.8% of C_8H_{18},
23.6% of C_4H_{10}, and 19.4 mole % of C_2H_6. **229.** 2.8 mole % each
of C_3H_6 and H_2, and 47.2 mole % each of C_2H_4 and CH_4. **231.** 18.8
mole % of cumene, and 3.1 mole % of diisopropylbenzene. **232.** 26.0
mole % of C_3H_6, 32.5% of C_6H_{12}, and 41.5 mole % of C_9H_{18}.

Chapter 5

233. (a) 40.2 atm; 59.2 atm. **234.** By the first method $f_{100} = 91.5$ atm, and $f_{500} = 628$ atm. **235.** By the graphical method through α: 102.3 and 548 atm. **236.** By Eq. (5.1): 54.2 atm. **237.** 58.5 atm. **238.** (a) 106.6 atm; 2415 atm. **239.** According to volume correction α: $f_{100} = 99.3$ atm, and $f_{300} = 261$ atm. **240.** By Eq. (5.1) $f = 51.5$ atm. **241.** 33.2 atm. **242.** 32.7 atm. **243.** 138 atm. **245.** According to the Forman and Thodos method (T_{cr}, K and p_{cr}, atm, respectively): (1) 621, 28.8; (2) 220, 35; (3) 465, 36.5; (4) 806, 61.6; (5) 764, 30.1; (7) 660, 31.9; (8) 650, 19.8; (9) 690, 37.5; (10) 589, 30.2; (11) 666, 29.5; (12) 675, 24; and (14) 590, 47.8. According to Lydersen's method: (6) 511, 40.5; and (13) 750, 45.5. **246.** 29 mole % each of C_2H_4 and C_4H_{10}, 42 mole % of C_6H_{14}. **247.** 7.2 mole % of n-heptane. **248.** (In mole %) $C_6H_5CH_3$—7, H_2—21.0, and $C_6H_{11}CH_3$—72. **249.** 46.8 mole %. **250.** 44.5 mole % each of C_2H_4 and H_2O, 11.0 mole % of C_2H_5OH. **251.** 100 mole %. **252.** (In mole %) C_3H_4—5.7, H_2—11.5, and C_3H_8—82.8. **253.** About three times, up to 3.5 mole %. **254.** 90 mole %. **255.** (In mole %) C_4H_{10}—49.1, C_3H_8—49.1, H_2—1.2, and $C_6H_{11}CH_3$—0.6. **256.** 48.25 mole %. **257.** (In mole %) C_9H_{20}—1.9, CH_4—25.7, C_5H_{10}—25.7, C_2H_6—5.1, C_3H_8—1.9, C_2H_4—1.9, C_3H_6—30.8, and C_4H_8—7. **258.** (In mole %) C_4H_{10}—75, C_2H_4—0.3, neohexane—16.5, and 2,2-dimethylbutane—8.2. **259.** (In mole %) C_3H_8—4.7, CH_4—48.77, C_2H_4—44.26, isobutene—0.89, 1-butene—0.45, cis-2-butene—0.39, and trans-2-butene—0.54. **260.** No, it cannot. **261.** ($H - H_0$, cal/mol): (1) —2829; (2) —3190; (3) 4855; (4) 408; (5) 15 825; (6) 5940 (vapour), 3210 (liquid); and (7) 7110. **262.** (I) —11 044 cal; and (II) —18 945 cal. **263.** No, we cannot. **264.** (kcal) (1) 20.3; (2) 39.485; and (3) 35.254. **265.** (1) 2.1%; (2) 2%; (3) 0%; and (4) 3%.

Combined Problems

266. 1.6 mole %. **267.** Above 450 K. **268.** 47.68% of styrene and 2.3% of α-methylstyrene. **269.** (In mole %) α,α'-dinitronaphthalene—46.8, α,β'-dinitronaphthalene—3.2, and H_2O—50. **270.** 32.5 mole %. **271.** At any temperature. **272.** (1) $\Delta G^\circ/T = 41.6 - 9.5 \log T - 0.03T + 2.72$; (2) (in mole %) Cl_2—28.2, H_2O—28.2, O_2—14.6, and HCl—29.0; (3) (in mole %) Cl_2—45.4, H_2O—45.4, O_2—3.0, and HCl—6.2. **273.** The first and the second reactions. **274.** (In mole %) (2) H_2—26.5, SO_2—8.8, H_2S—21.5, and H_2O—43.2; (3) H_2—10.8, SO_2—3.5, H_2S—28.2, and H_2O—57.5. **275.** 15.6 mole % of the primary and 9.4 mole % of the secondary alcohols. **276.** The second and the third reactions. **277.** The first and the second reactions. **278.** 69 mole %. **279.** The content of acetone in the equilib-

rium mixture will grow from 95.6 to 97.1 mole %, while the content of mesityl oxide will drop. **280.** 21 mole %. **281.** The first and the third processes will give the greatest yield—12.5 mole % each per mole of CH_4 or $(CH_3)_2CO$. **282.** 27 mole %. **283.** By 3 mole %. **286.** No, it is not. **287.** 66.4 mole %. **288.** 48.5 mole %. **290.** (In mole %) at 600 K—4.0% of mono- and 27.0% of dimethyl aniline; at 700 K—8.0% of mono- and 16.3% of dimethyl aniline; and at 800 K—8.6% of mono- and 8.0% of dimethyl aniline.

TO THE READER